

Diffusion Coefficient of Ethylene in NMP Using Pressure Decay Method: Experimental and Modelling Study

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ABSTRACT: *The pressure decay of ethylene due to diffusion into the stagnant liquid of N-methyl-2-pyrrolidone (NMP) is evaluated at temperatures of 278.15, 298.15, and 328.15 K, and at three initial pressures of about 0.6, 0.8, and 1.1 MPa. Then, an available graphical method named the initial model is implemented to calculate the diffusion coefficient. Some corrections on the initial model are applied as follows: 1) in the infinite series of the solution to Fick's second law, more terms are considered. 2) the equilibrium pressure is considered a tuning parameter to eliminate the requirement for an inaccurate experimental measurement. The proposed model is proven to be more reliable and valid for a whole range of pressure decay data including the early times. Due to the large differences between the results of the initial and the proposed models, the Wilke-Chang relation is considered a basis for comparison. This comparative study shows that the results of the Wilke-Chang relation are more compatible with the proposed model.*

KEYWORDS: *Molecular diffusion coefficient; Pressure decay; Fick's second law; Ethylene.*

INTRODUCTION

Due to its utilization as a main raw material, ethylene is one of the valuable products of petrochemical industries. Ethylene is customarily produced using steam cracking, catalytic cracking, and catalytic dehydrogenation of paraffin [1] in which a considerable amount of ethane, propylene, and propane are produced as by-products. According to similar physical and chemical properties, cryogenic distillation is traditionally used to purify ethylene up to required purity in downstream units (99.9%) [2]. However, because of high capital and operating cost, this method is a highly energy-intensive process [3]. Therefore, finding a suitable replacement for cryogenic distillation has been an attractive task recently [4, 5] and in former times [6].

The operations based on the solution and diffusion of ethylene in a proper solvent such as gas absorption and gas-liquid membrane contactors were severally investigated as a replacement for cryogenic distillation and the performance of different solvents was evaluated [5,7]. In these methods, the molecular diffusion as well as the solubility, play an important role in the ethylene purifying process.

When a gas is brought into contact with a solvent, the diffusion occurs in the stagnant liquid film near the interface. Therefore, the diffusion controls the transfer rate of species in gas-liquid separation operations [8]. Molecular diffusion has received great attention as a basic mechanism for the separation and recovery of crude oil in most of the

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petroleum processing and also, similar carbon number olefin/paraffin separation [9, 10].

Generally, two methods are used to measure the molecular diffusion coefficient:

Direct method: In this method, the concentration of diffusing gas in the liquid is measured using some experimental methods like GC, and the molecular diffusion coefficients are then calculated from the gas concentration profile. Due to the various sampling and analysing steps required, this method may be complicated and expensive. Moreover, the sampling step may exert some disturbances in the system.

Indirect method: In this method, the molecular diffusion coefficient is calculated by recording the variation of some physical properties of diffusing gas like pressure, temperature, and volume by which the gas solubility can be determined. Researchers are more interested in this method due to the reduced cost of experiments, minimized errors of measurement, simplicity of the experimental design, shorter time of experiment, and easy application for a wide range of pressures [11].

Among the indirect methods for the calculation of the molecular diffusion coefficient, the pressure decay method is preferred due to its simplicity and accuracy [12, 13]. In this method, the system is considered stagnant in a PVT cell during mass transfer of the gas to the liquid phase. Mathematically, a relation exists between the rate of the pressure decay and the rate of the gas diffusion into the liquid phase in the constant-volume cell. Accordingly, the concentration of the diffusing gas in the liquid phase can be obtained from the gas phase pressure decay. In all of the previous studies on this method, the experimental procedure was nearly the same and the difference was related to the assumptions, mathematical calculations, and modelling of gas diffusion behavior in liquid. As the molecular diffusion coefficient is tuned by correlating the pressure decay data with the developed mathematical model, one of the important challenges for the precise calculation is choosing a proper mathematical model.

Riazi [8] who has employed this method for the first time, related the pressure decay rate, liquid phase swelling, and gas/liquid interface velocity with the rate of gas diffusion at constant temperature and volume. In his method, the molecular diffusion coefficient was calculated from the simultaneous solution of diffusion equations in liquid and gas phases.

Zhang [14] developed their own approach using the method suggested by *Riazi* [8] neglecting the liquid swelling, and relating the diffusion equation with equilibrium relation on the gas/liquid interface. In their method, the compressibility factor was constant, the liquid phase swelling was ignored, and the molecular diffusion coefficient was considered as a tuning parameter. According to their physical and mathematical assumptions, a graphical method was developed which simply predicted the diffusion coefficient. The final equilibrium pressure was one of the physical parameters required in this calculation method. Due to the very long-term process of the gas diffusion in a stagnant liquid, it was very difficult to obtain the precise value of equilibrium pressure in a pressure decay test and this was the main constraint in presenting the exact results. Moreover, the authors stated that the calculated diffusion coefficient was very sensitive to the value of equilibrium pressure. The most important benefit of a graphical method is its simplicity and that the diffusion coefficient can be obtained rapidly without any iteration.

Civan [15] and *Rasmussen* [16] developed a mathematical model on the basis of the experiments performed by *Zhang* [14] at the equilibrium and non-equilibrium conditions. They concluded that the accuracy of the results was related to the assumptions considered for simplifying the solution of the mathematical equations.

Upreti and *Mehrotra* [17] suggested a numerical approach based on pressure decay data for the calculation of the molecular diffusion coefficient as a function of the concentration. *Sheikha* [18] presented a graphical method for the calculation of the molecular diffusion coefficient using the experimental data of *Upreti* and *Mehrotra* [17]. In their model, the diffusion behavior was different at the initial and final stages of the operation. Their method could detect some of the data presumed to be under undesirable conditions of the experiments. They calculated the molecular diffusion coefficient using initial points of pressure decay data and then, suggested a method for direct estimation of the molecular diffusion coefficient.

Creux [19] designed two different experiments for the measurement of the molecular diffusion coefficient of methane in heavy oil. In the first experiment, their calculations were based on pressure decay experimental data obtained from a PVT cell. In the second experiment, the molecular diffusion coefficient was measured

by evaluating the concentration profile of methane molecules. They eventually concluded that the molecular diffusion coefficient in heavy oils is much less than that in ordinary oils.

Tharanivasan [20, 21] used three different boundary conditions including equilibrium, pseudo equilibrium, and non-equilibrium for the calculation of the molecular diffusion coefficient. They compared their own results with the study of *Zhang* [14] and concluded that the non-equilibrium boundary condition was more suitable for CO₂/heavy oil, and the equilibrium boundary condition for methane/heavy oil. *Azizi* [22] measured the molecular diffusion coefficient of propylene in NMP using pressure decay approach. The absorption system was simulated using Fick's second law, and three distinct regions affecting the kinetic behavior of the system were identified.

Zhang [23] studied the diffusion of CO₂ in brine at the equilibrium condition. They also suggested a simple method for the calculation of the molecular diffusion coefficient. They showed that increasing temperature and pressure and decreasing the saturation concentration increase the molecular diffusion coefficient.

Etminan [24] studied the effect of gas/heavy oil interface resistance on the molecular diffusion coefficient. *Kavousi* [25] investigated the solubility of CO₂ in two types of heavy oils with different viscosities using pressure decay method. Their results showed that increasing the initial pressure enhanced the gas solubility, and also increased the molecular diffusion coefficient in heavy oil. Indeed, increasing temperature increased the molecular diffusion coefficient, too.

Gholami [26] used the pressure decay method to calculate the molecular diffusion coefficient of CO₂ in water. They believed that using earlier initial data points in the pressure decay test for tuning the diffusion coefficient value may lead to more precise results.

Gholami [27] studied the solubility and diffusivity of CO₂ in NMP. They observed that the molecular diffusion coefficient increased with increasing temperature and pressure. *Yang* [28] developed a rigorous pseudo-equilibrium model on the basis of pressure decay data for the calculation of the molecular diffusion coefficient. They compared their results with the results of equilibrium models and concluded that their model contains less error than the equilibrium models.

Pacheco Roman and *Hejazi* [29] proposed a new graphical procedure based on pressure decay experiments to estimate the interface mass transfer coefficient and diffusion coefficient of gases in heavy oil. *Xu* [30] obtained oxygen diffusion coefficients in gas-liquid systems by using two different mathematical approaches based on the probability and statistics theory. Although these two methods were implemented in different experimental systems, the diffusion coefficients of oxygen dissolved in water calculated from the two measurements were very close. *Comite* [31] studied the diffusion of carbon dioxide into aqueous solutions of different absorbents. Their model included the governing equations that were a function of the physical and chemical parameters like Henry's law constant, diffusion coefficients and reaction rates.

As can be seen, researchers used different models for the determination of the molecular diffusion coefficient of various gases in different liquids. Some of these models are applicable to specific conditions and have their own restrictions. Therefore, it is necessary to evaluate the validation of these models under different conditions. Most of the presented models in the literature are complicated and a long time is required for iteration and optimization. However, the graphical models are simpler and the diffusion coefficient can be obtained after a short calculation. The aim of this experimental study was to calculate the molecular diffusion coefficient of ethylene in NMP using the pressure decay method. Due to its simplicity and no need for iteration, the graphical method presented by *Zhang* [14] is used to predict the diffusion coefficient of ethylene in NMP. However, owing to some shortages appeared in implementing the *Zhang* method, a new mathematical method is also developed to predict the pressure decay behavior of the system and the diffusion coefficient as well. Finally, the results of two models are compare to each other.

EXPERIMENTAL SECTION

Materials

All chemicals were used as purchased without further purification. N-methyl-2-pyrrolidone (C₅H₉NO, 99.8 wt.%) and ethylene (99.98 mol.%) were provided by Amirkabir Petrochemical Co. in Iran. NMP which is widely used as a solvent in petrochemical industries, is an organic liquid with sever polar properties and amine like odour.

Due to its low vapor pressure (0.5 mm Hg at 298 K) compared to water (23.8 mm Hg at the same temperature) and high normal boiling point (475 K) it can be considered as a non-volatile solvent [13].

Experimental setup and procedure

Fig. 1 shows a schematic of the experimental setup used for pressure decay tests. It consists of an intermediate cell with the capacity of 500 mL, and an absorption cell with the capacity of 370 mL. These two cells are connected using appropriate piping. An isolation valve is mounted between the cells to open or close the line. A PT-100 Ω type temperature sensor with the accuracy of 0.1 K is positioned in the absorption cell to show the solvent temperature, which is completely immersed in the liquid phase. A pressure sensor model PSCH0025BCIJ of Sensys Co. with the accuracy of 0.001 MPa is used to show the gas phase pressure. For temperature control, all system components including the intermediate cell, the absorption cell, and the connections are submerged in a constant temperature water bath. Initially, 100 mL of the NMP is poured in the absorption cell and the cap is closed. Under the flanged door of the absorption cell, a mesh with suitable size is used, which pursues two aims: 1) Uniform distribution of the injected gas, and 2) Preventing the injected gas from jetting on the surface of the solvent and making it turbulent. According to the geometry of the absorption cell, the height of liquid in the cell (x_0) is equal to 0.0331 m. When the vacuum pump is connected and the gas phase is evacuated, the ethylene is injected to the intermediate cell while the isolation valve is closed. The injection continues until the pressure reaches a predetermined value (one of 0.6, 0.8 or 1.1 MPa). A few minutes is required to ensure that the temperature of the gas is equal to that of water bath during which the pressure of the intermediate cell may slightly change. Then the pressure of the intermediate cell (P_{int}) is recorded. In addition to the temperature control, the intermediate cell helps to record the pressure of the charged gas before any absorption occurs, and as a result, the initial amount of the injected gas could be calculated more precisely. Then the isolation valve opened and the gas is conducted to the absorption chamber. At the same time, the pressure of the system is also recorded as the initial pressure (P_i). According to different experimental constraints, this value may be about 0.02 MPa more or less than the planned initial pressure.

The pressure drop of the systems due to the absorption is also recorded regularly during 12 h period to obtain kinetic curve of pressure decay experiment.

It is noted that the experiments must be performed without any mixing or turbulence or movement of the fluids since the diffusion must be the only governing mechanism of mass transfer. Moreover, for the measurement of Henry's law constant and equilibrium pressure, all of the experiments are repeated in the presence of mixer to reach the equilibrium in a reasonable time. Before each experiment, the system is checked against any leakage and all measuring instruments including temperature and pressure sensors are calibrated. The experiments are planned to perform at three temperatures of 278.15, 298.15, and 328.15 K, and three initial pressures of about 0.6, 0.8, and 1.1 MPa.

MODELLING

Fig. 2 demonstrates the absorption cell and the origin and axis of the coordinates. As previously stated, the NMP vapor pressure is low enough to ignore its vaporization loss at the operating conditions of this research [22]. Therefore, the gas phase can be considered pure.

After the initial contact between the gas and the liquid, the gas is dissolved in the liquid interface. This creates a concentration gradient along the liquid column, and hence, diffusion started. Therefore, at any moment, the ethylene concentration reached its highest value at the interface and decreases as it moves downwards.

Even if the dissolution process makes a considerable density gradient, the lower density liquid is placed at the top and the higher density at the bottom of the solvent column. Therefore, no free convection of the liquid inside the cell is expected. However, according to the low solubility of ethylene in NMP, the density changes and also the volume expansion of the liquid can be ignored.

Assuming that the molecular diffusion coefficient is independent of the concentration, and there is no reaction between solute and solvent, Fick's second law can be used as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where C is the gas concentration in liquid, D is the molecular diffusion coefficient, t is time, and x is the axial position in liquid column.

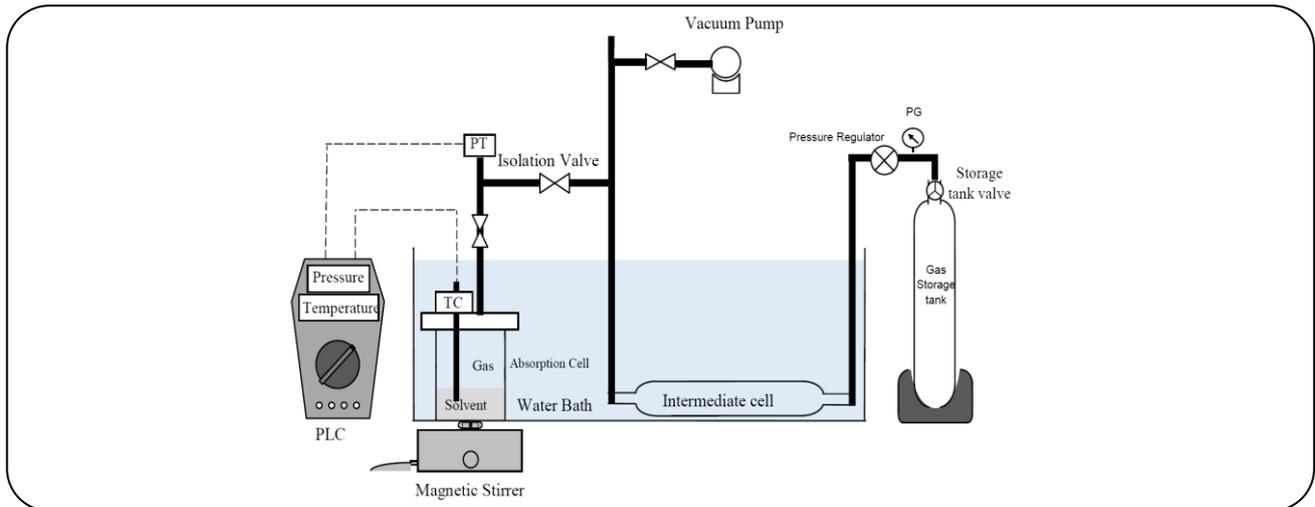


Fig. 1: Schematics of the experimental setup used in this study.

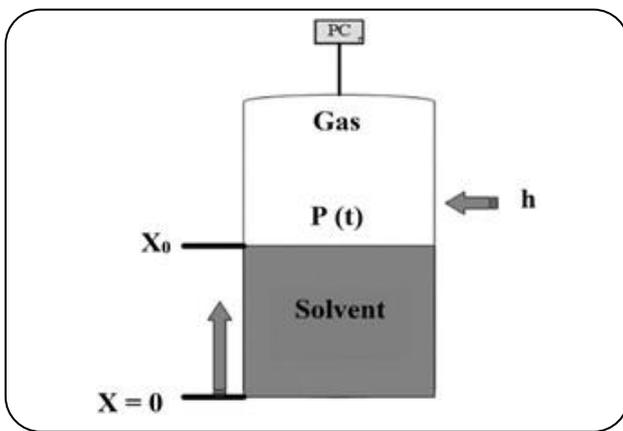


Fig. 2: Illustrative boundary conditions of the absorption cell.

Initially ($t=0$), as soon as the gas comes into contact with the liquid, the concentration in the whole liquid is zero except for the interface. Thus, the initial condition can be written as follows:

$$C(x, 0) = 0 \quad 0 \leq x < x_0 \quad (2)$$

Ignoring the interface resistance, it can be assumed that the interface is at the equilibrium state. It means that the concentration at the interface at any time is a function of gas pressure at that time, and can be obtained from the equilibrium curve of the system under study.

$$C(x_0, t) = C^* \quad (3)$$

where C^* is the equilibrium concentration at the interface at any time.

As the gas pressure is changing continuously with time, C^* also changes as a function of time. However,

considering the small variation of gas pressure during a pressure decay test of the ethylene-NMP system, the variation of C^* which is nearly 10% at most, can be ignored and it is considered a constant value. This assumption makes the analytical solution easier.

At the bottom of the cell, the diffusion terminated and insulation boundary condition is applied:

$$\left(\frac{dC_A}{dx}\right)_{x=0} = 0 \quad (4)$$

Considering the above assumption, Crank [AZ1][32] solved Eq. (1) as follows:

$$C = C^* - \frac{2C^*}{x_0} \sum_{n=0}^{\infty} (-1)^n \lambda_n \cos(\lambda_n x) \exp(-\lambda_n^2 Dt) \quad (5)$$

$$\lambda_n = \frac{(2n+1)\pi}{2x_0}$$

The initial model

In this study, the graphical method proposed by Zhang [14] is implemented for calculation of the molecular diffusion coefficient of ethylene in NMP. As mentioned before, the graphical methods are interesting because they don't require try and error. This method is based on the mass balance at the interface. Assuming that there is no accumulation of gas molecules at the interface, number of moles of entering gas to the interface must be equal to those passing the interface by the mechanism of the molecular diffusion.

$$-\frac{V}{ZRT} \frac{dP}{dt} = \left(DA \frac{\partial C}{\partial x} \right)_{x_0=x} \quad (6)$$

where V is volume of the gas, R is universal gas constant, T is the temperature of the experiment, A is contact area of gas/liquid in the cell and Z is gas compressibility factor at the operating condition and obtained using Peng-Robinson EOS. In the pressure decay range the compressibility factor is considered constant.

By integrating from both sides of Eq. (6), we have:

$$\int_{P(t)}^{P_{eq}} dP = -\frac{DAZRT}{V} \int_t^{\infty} \left(\frac{\partial C}{\partial x} \right)_{x=x_0} dt \quad (7)$$

The upper limit of the left-hand side integral is the system pressure at the infinite time. This pressure can be the equilibrium pressure at the governing temperature and initial pressure. For $\frac{\partial C}{\partial x}$, the derivative of Eq. (5) with respect to x is used. Then, the integration results in Eq. (8):

$$P(t) - P_{eq} = \frac{2C^*AZRT}{x_0V} \sum_{n=0}^{\infty} \frac{1}{\lambda_n^2} \exp(-\lambda_n^2 Dt) \quad (8)$$

Zhang [14] stated that for large values of t , only the first term of the infinite series is considerable. By ignoring the other terms, they developed a model for the variation of pressure with time as follows:

$$P(t) - P_{eq} = \frac{4x_0C^*AZRT}{\pi^2V} \exp\left(-\frac{\pi^2D}{4x_0^2}t\right) \quad (9)$$

Rearranging Eq. (9):

$$\ln(P(t) - P_{eq}) = \ln\left(\frac{4x_0C^*AZRT}{\pi^2V}\right) - \frac{\pi^2D}{4x_0^2}t \quad (10)$$

Finally, by plotting $\ln[P(t) - P_{eq}]$ against time and obtaining the slope of the line, the molecular diffusion coefficient is obtained.

Proposed model

In this study, in order to increase the accuracy of the model, more terms are considered in Eq. (8) instead of the first term only. On the other hand, obtaining the exact equilibrium pressure is not possible in a pressure decay experiment, thus, in the proposed model P_{eq} is considered as an unknown function. As stated before, to obtain the analytical solution, C^* is considered constant. Despite such assumption, it is basically a time-dependent parameter. For numerical operations, the average value of

the variable is commonly substituted. However, in the proposed model, the instantaneous C^* is implemented. On the basis of Henry's law, this parameter is related to the operating pressure according to Eq. (11)

$$C^* = \frac{P(t)}{H} \quad (11)$$

where H is Henry's law constant. Therefore, Eq. (8) can be re-arranged as follows:

$$P_c(t) = \frac{P_{eq}}{1 - \frac{2AZRT}{x_0VH} \sum_{n=0}^{N-1} \frac{1}{\lambda_n^2} \exp(-\lambda_n^2 Dt)} \quad (12)$$

where N is the number of the terms in the infinite series considered for the calculation of the diffusion coefficient. Subscript c indicates the calculated instantaneous pressure.

The deviation of the calculated pressure from the experimental one is obtained from Eq. (13):

$$A. A. D\% \left(\frac{100}{M} \right) \cdot \sum_{i=1}^M \frac{|P_c(t_i) - P(t_i)|}{P(t_i)} \quad (13)$$

where M is the number of data points in the pressure decay test. The values of D and P_{eq} in Eq. (12) are varied so that the deviation defined in Eq. (13) reaches its minimum value.

In this regard, the optimum values of D and P_{eq} can be obtained. In this study, D is changed in the range of 1×10^{-11} to 1×10^{-8} m²/s with the step size of 10^{-11} m²/s, and P_{eq} is changed in the range of experimental final pressure and 0.2 MPa lower than that with the step size of 0.001 MPa. To find the optimum point with minimum deviation with the experimental pressure decay data, a MATLAB code is developed. Fig. 3 shows the algorithm of the proposed model.

Wilke and Chang [33] proposed a relation for the prediction of the molecular diffusion coefficient of gases in liquids for dilute and non-electrolyte systems:

$$D_{AB} = \frac{117.3 \times 10^{-18} (\varphi M_B)^{0.5T}}{V_A^{0.6} \mu} \quad (14)$$

where D_{AB} is the molecular diffusion coefficient (m²/s), μ is solvent viscosity (Pa.s), V_A is molar volume of the solution at its normal boiling point (m³/kgmol), M_B is molecular weight of solvent (kg/kgmol), T is absolute temperature (K), and φ is association factor of the solvent.

The values of the molecular diffusion coefficient of ethylene in NMP was calculated considering $\varphi=1$.

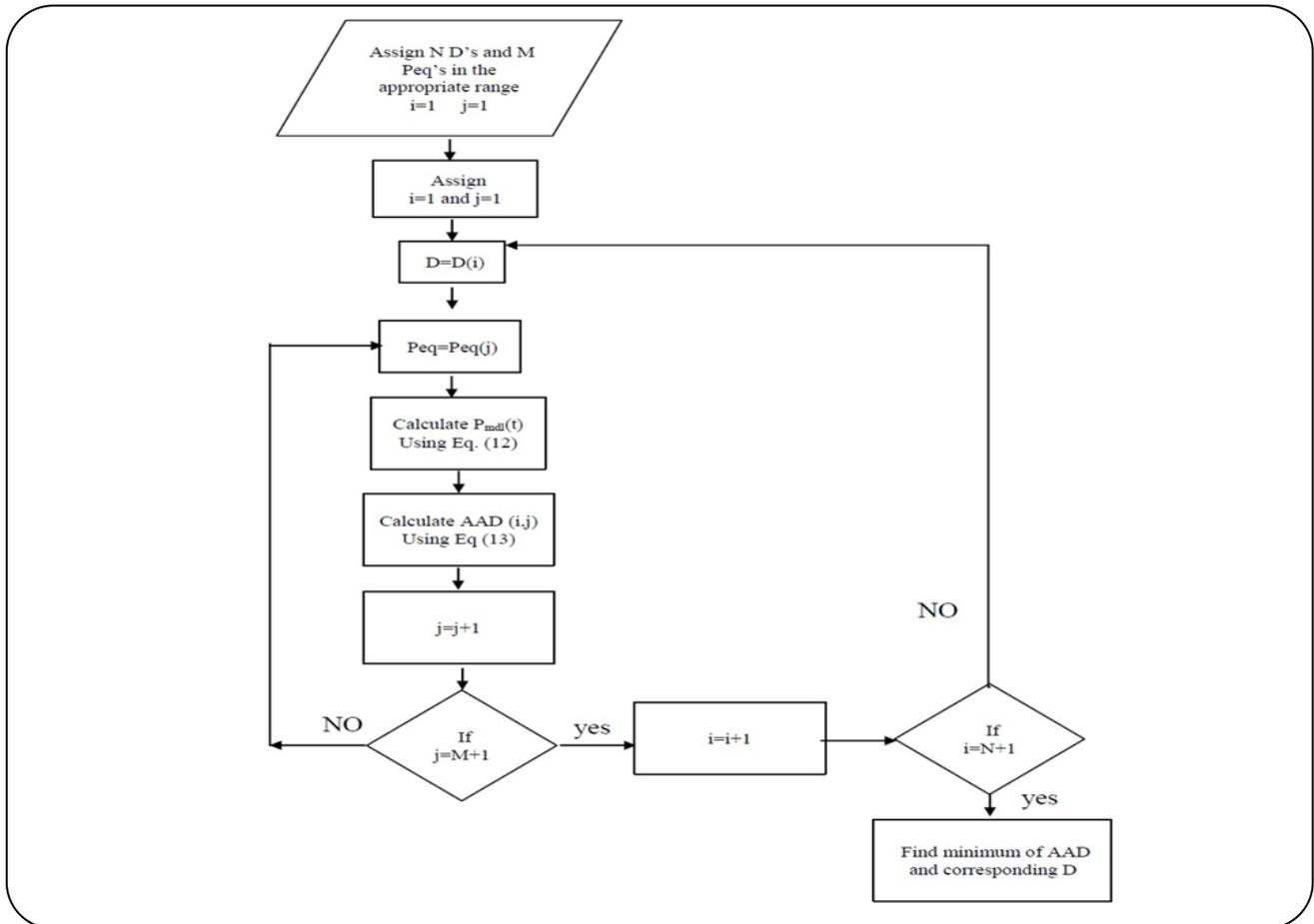


Fig. 3: The algorithm of the proposed model.

The deviation of prediction of Wilke-Chang correlation from the experimental diffusion coefficient obtained in this study was calculated as follows:

$$\text{dev}(\%) = 100 \times \frac{|D_{AB}^{WC} - D_{AB}|}{D_{AB}^{WC}} \quad (15)$$

Since Wilke-Chang relation is basically restricted to dilute systems, the most dilute solution of ethylene in NMP at the initial pressure of about 0.6 MPa is considered for the comparison with the Wilke-Chang results.

The main problem of the original Zhang model is its sever sensitivity to the value of equilibrium pressure. Since very long time needed to reach the exact amount of equilibrium pressure in the experiment, in the proposed model, this pressure is considered as one of the unknown parameters of the system which can be calculated *via* model. In this regard, the optimal amount of equilibrium pressure as well as the amount of molecular diffusion coefficient can be calculated simultaneously. On the other

hand, in the original Zhang model, two sentences from an infinite series are used, and as we know, the more the number of sentences in the infinite series used in calculations, the more the accuracy of the calculations would be. The proposed model has the ability to use infinite sentences from the infinite series and thus optimize the value of the molecular diffusion coefficient in the solvent.

RESULTS AND DISCUSSION

Solubility data

Since the equilibrium pressure must be a known term in the initial model, some experiments are performed at the similar operating conditions using a mixer to reach the equilibrium pressure rapidly. Table 1 shows the values of the equilibrium pressures obtained in this study. The solubility of ethylene in NMP at different temperatures and pressures can be obtained using the initial and equilibrium pressures accompanied with Eq. (16). Details of this method are explained in [13].

$$C = \frac{V}{RT} \left(\frac{P_i}{Z_i} - \frac{P_{eq}}{Z_{eq}} \right) \cdot \frac{1}{V_l} \quad (16)$$

where V_l is the liquid volume which can be considered as the initial volume of the solvent ignoring the liquid expansion during absorption process.

Fig. 4 demonstrates the equilibrium curves of ethylene/NMP system at three different temperatures. Although Henry's law constant is commonly defined for solubility's of less than 3 mol.% [34], due to the good linear trend of equilibrium data, all of them are used to evaluate the Henry's law constant. Henry's law constants found from the slopes of the fitted lines are used in the next stages of modelling procedure.

The values of Henry's law constants are also reported in Table 1. The equilibrium data for ethylene-NMP system in a wider range of equilibrium pressures are also reported by *Yousefi* [35] which shows a good agreement with the equilibrium data obtained in this work.

Pressure decay data

According to the model requirement, the pressure decay data should be obtained when the solvent was completely stagnant. The experiments were performed at 278.15, 298.15, and 328.15 K, and three initial pressures of about 0.6, 0.8, and 1.1 MPa. These values are the nominal initial pressures. The actual initial pressures may be 0.02 MPa more or less than this nominal value. Fig. 5 shows the pressure-time curves at different temperatures in the absence of any mixing or agitation inside the liquid. No fluctuation in the curves indicates that system temperature was properly controlled during the experiments. As can be seen, all data were recorded during 12 h.

The equilibrium condition will be obtained when no change in pressure over time is observed. These profiles show that as expected, pressure has decreasing trend with time but never reached the equilibrium state. In no-mixing cell, depending on the type of materials, it may take several weeks to reach the actual equilibrium pressure.

Initial model

Having the equilibrium pressure, the linear curve fitting according to Eq. (10) is performed and presented in Fig. 5. From the slopes of the fitted line, the values of the molecular diffusion coefficients are calculated at different operating conditions. Table 2 compares the calculated values of the molecular diffusion coefficients using the

Table 1: Experimental values of equilibrium pressure and Henry's law constant.

T (K)	H (MPa.m ³ /mol)	R ²	P _i (MPa)	P _{eq} (MPa)
278.15	0.00157	0.99	0.605	0.513
			0.812	0.689
			1.118	0.951
298.15	0.00174	0.99	0.614	0.518
			0.811	0.695
			1.109	0.962
328.15	0.00216	0.96	0.602	0.53
			0.804	0.712
			1.1	0.966

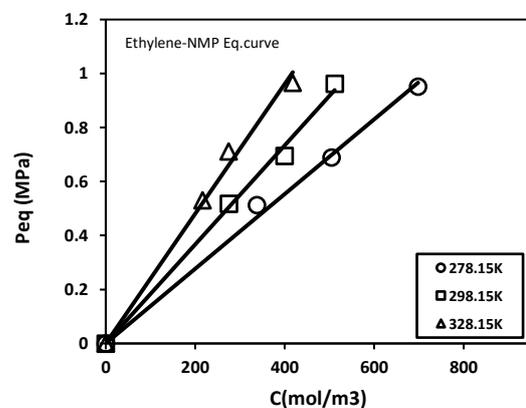


Fig. 4: Equilibrium curve for ethylene/NMP at three different operating temperatures.

initial and the proposed models. The deviations of the predictions of these two models are also reported in Table 2. Since only the first term of the infinite series is considered in the initial model, this model is more valid at large t . Therefore, the experimental pressure decay data for $t < 1$ h are not considered in the calculations in order to have a better fitting of Eq. (10) and increase the accuracy of the results of the initial model.

As can be seen in Fig. 6, the experimental data at 278.15 K have a very good linear trends while at two other temperatures, some data sets have considerable deviations from linear behavior.

Our analysis reveals that if the equilibrium pressure changes slightly, better linear trend would be obtained. For instance, this subject is analysed for the temperature of 328.15 K and the initial pressure of 1.1 MPa in Fig. 7.

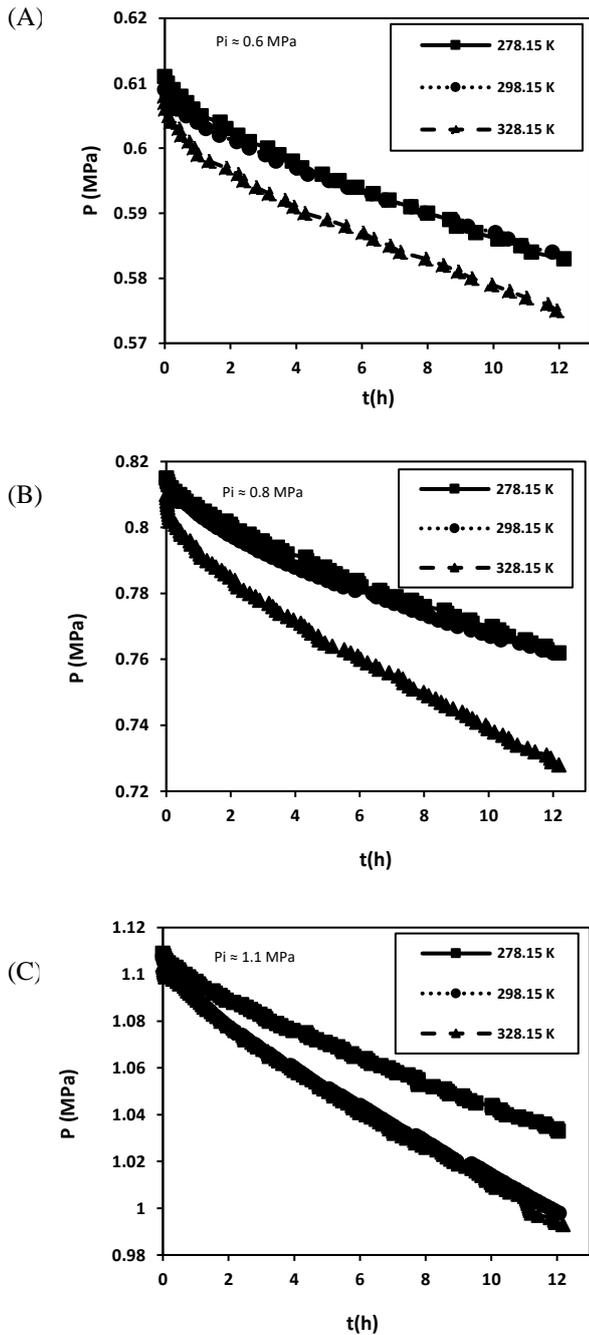


Fig. 5: Pressure decay curves for ethylene absorption in NMP at different temperatures and initial pressure of (A) 0.6 MPa, (B) 0.8 MPa, (C) 1.1 MPa.

It is obvious that by changing the equilibrium pressure from 0.966 MPa (the equilibrium pressure measured in this study) to an arbitrary value of 0.9 MPa, the curve of $\ln[P(t) - P_{eq}]$ show a more linear trend. This small change in the equilibrium pressure not only increases the coefficient of determination (R^2) but also gives very

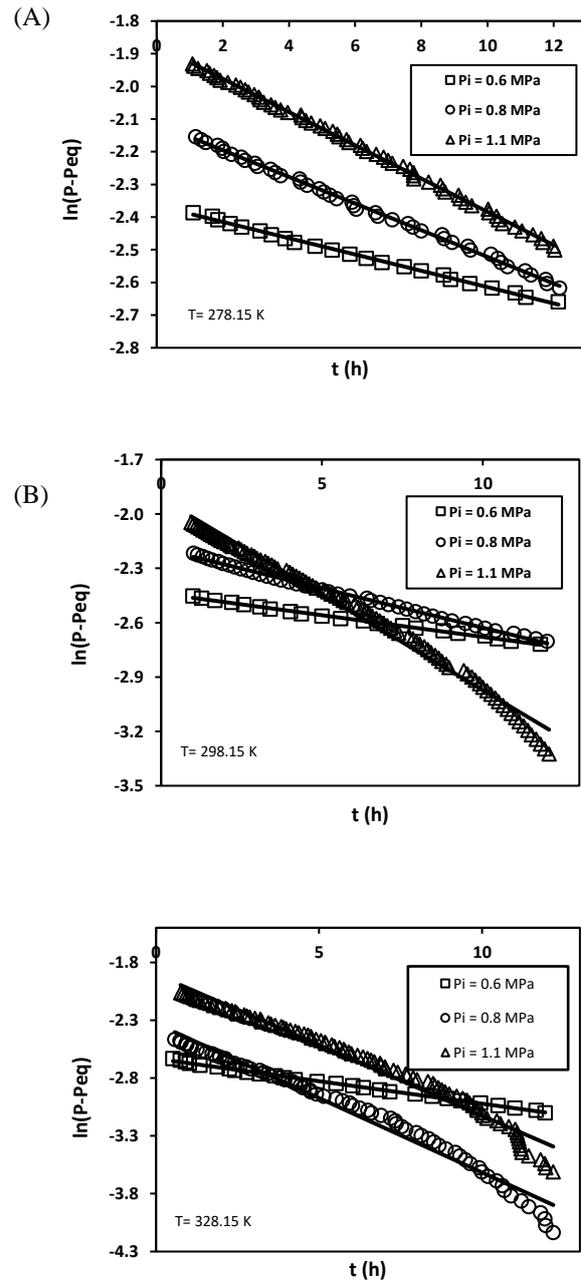


Fig. 6: Logarithmic pressure decay against time at the temperature of (A) 278.15 K, (B) 298.15 K, (C) 328.15 K.

different value for the molecular diffusion coefficient. This may be due to the fact that determination of the equilibrium pressure has some inherent errors.

The initial pressure or the liquid volume in the cell in the equilibrium tests and the pressure decay experiments may not be exactly the same. Thus, the value obtained

Table 2: The values of the molecular diffusion coefficients of ethylene in NMP solvent obtained from the two models in comparison with Wilke-Chang relation.

Test No.	Nominal P _{ini} (MPa)	T (K)	Initial Model				Proposed Model			
			D×10 ⁹ (m ² /s)	P _{eq} (MPa)	A.A.D. (%)	dev. (%)	D×10 ⁹ (m ² /s)	P _{eq} (MPa)	A.A.D. (%)	dev. (%)
1	0.6	278.15	3.04	0.513	0.12	73.8	1.04	0.48	0.06	3.8
2		298.15	2.88	0.518	0.11	55.5	1.61	0.516	0.06	0.0
3		328.15	4.63	0.53	0.18	54.3	2.14	0.51	0.09	7.3
4	0.8	278.15	4.35	0.689	0.11	-	1.70	0.651	0.11	-
5		298.15	5.28	0.695	0.16	-	3.75	0.691	0.09	-
6		328.15	16.2	0.712	0.45	-	7.06	0.682	0.32	-
7	1.1	278.15	5.24	0.951	0.07	-	1.82	0.888	0.16	-
8		298.15	12.90	0.962	0.27	-	8.90	0.948	0.33	-
9		328.15	15.05	0.966	0.45	-	9.16	0.944	0.4	-

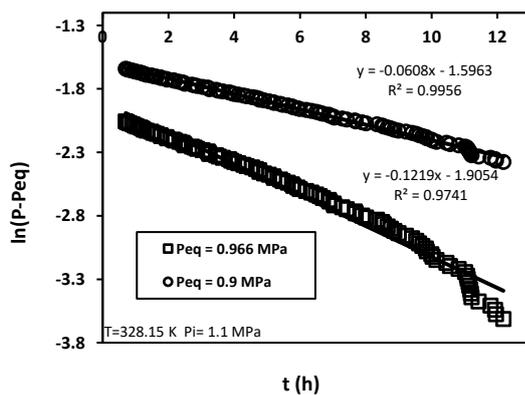


Fig. 7: Effect of equilibrium pressure on the accuracy of the initial model.

in the equilibrium tests may not be the same as the one obtained in the pressure decay test at infinite time. Therefore, it can be concluded that the molecular diffusion coefficient is very sensitive to the equilibrium pressure in the initial model which sounds as a considerable weakness of this method.

Another drawback of the initial model is to neglect the second term onwards in the infinite series of Eq. (8).

A parameter (ψ) is defined as Eq. (17) to make clear the error induced by this simplification.

$$\psi = \frac{\sum_{n=N}^{\infty} \frac{1}{\lambda_n} \exp(-\lambda_n^2 Dt)}{\sum_{n=0}^{\infty} \frac{1}{\lambda_n} \exp(-\lambda_n^2 Dt)} \times 100 \quad (17)$$

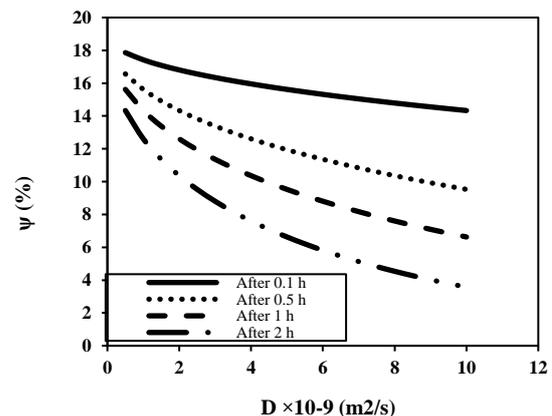


Fig. 8: Values of ψ versus diffusion coefficient at different time instances.

where N is the number of implemented terms in the infinite series, which is equal to unity in the initial model.

This parameter is defined as the ratio of sum of the removed terms in the model to sum of the total terms. At each time, the value of ψ only depends on the value of diffusion coefficient. Fig. 8 depicts the variation of ψ versus diffusion coefficient at various time instances.

It can be seen that at initial times of the pressure decay test, considering only the first term (according to the initial model procedure) may lead to a considerable error in the prediction of the diffusion coefficient. For example, 0.1 h after the first gas – liquid contact, depending on the value of the diffusion coefficient, the value of ψ , i.e.,

the contribution of the neglected terms in the total summation, is between 15% - 18%. However, an hour after the first contact, this value is reduced to 7%-16%. From Fig. 8 it can be concluded that this error can be reduced by neglecting more pressure decay data points at the early times. However, the number of data points that should be ignored is vague, and probably depends on the operating conditions. Therefore, it is not easy to decide about this problem. Besides, it should be noted that at the initial times of the experiment, the mechanism of the diffusion is the governing mechanism for gas uptake. Gradually and as time passes by, the solubility becomes more important in the absorption process [22]. Therefore, the validity of the diffusion equation (Eq. 1) which is the starting point in the initial model weakens over time. In conclusion, the neglect of several more pressure decay data at the early times is not an appropriate way for improving the linearization.

Proposed model

The developed model in this study is aimed to address the mentioned problems in the initial model. For this purpose, equilibrium pressure is calculated as a tuning parameter as well as diffusion coefficient, and more terms in the infinite series are considered in the calculations. Equilibrium pressure is changed within a suitable range (about 0.2 MPa) and for each equilibrium pressure, a value for the molecular diffusion coefficient is obtained by minimization of the error defined by Eq. (13).

Table 2 shows the values of the molecular diffusion coefficient calculated from the proposed model in comparison with the results of initial model. There is significant difference between the molecular diffusion coefficients of the initial model and proposed model. The proposed model is believed to have a stronger theoretical background; hence its results are more reliable.

Fig. 9 shows the molecular diffusion coefficient obtained from the proposed model at different operational conditions.

As can be seen, the molecular diffusion coefficient increases with increasing temperature and pressure. Although the diffusion coefficient of ethylene in NMP is rarely investigated, a similar effect of temperature on the diffusion coefficient is observed for other gas liquid systems [17,36]. Moreover, the well-known relations like Wilke-Chang correlation confirm that the diffusion coefficient increases by increasing temperature. However,

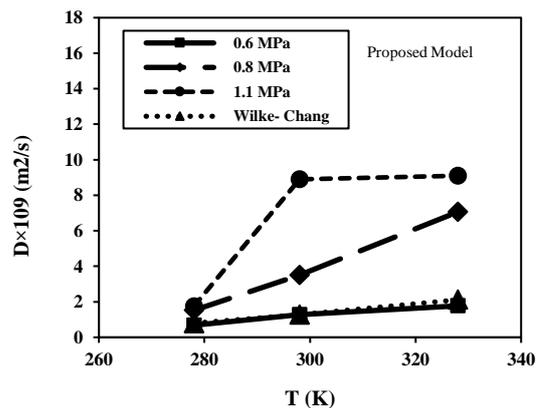


Fig. 9: The values of the molecular diffusion coefficient of ethylene in NMP at different operating conditions obtained from the proposed model

the effect of pressure on diffusion coefficient has not been established well and different observations were reported.

As stated before, in this work the diffusion coefficient increased by increasing pressure. A similar trend was reported in the work of Upreti and Mehrotra [17] in which the diffusion coefficient of CO₂ in bitumen increased by increasing pressure. The diffusion coefficient of CO₂ in brine in the work of Azin [37] also showed a similar trend. However, a contradictory result was reported for the system of CH₄ in bitumen [17] or CO₂ in propylene carbonate [36] where the diffusion coefficient decreased by increasing pressure. Therefore, it can be concluded that the effect of pressure on the diffusion coefficient depends on the characteristics of gas/liquid system.

The predictions of Wilke-Chang correlation were shown in Fig. 9 and the deviation of the calculated molecular diffusion coefficient by the two model from Wilke-Chang correlation was presented in Table 2. It is clear that the initial model did not show acceptable agreement with the Wilke-Chang model even for the initial pressure of about 0.6 MPa. On the other hand, according to Fig. 9 and Table 2, the proposed model fitted well with the Wilke-Chang at 0.6 MPa. However, at 0.8 and 1.1 MPa a great deviation is observed between the results of the proposed model and that of Wilke-Chang model. This behavior can be due to the fact that at higher pressures the system deviates from dilution state which is the essence of Wilke-Chang relation. Once again, this proved that the results of the proposed model are more reliable.

It should be noted that, in order to find the minimum number of required terms in the infinite series to save

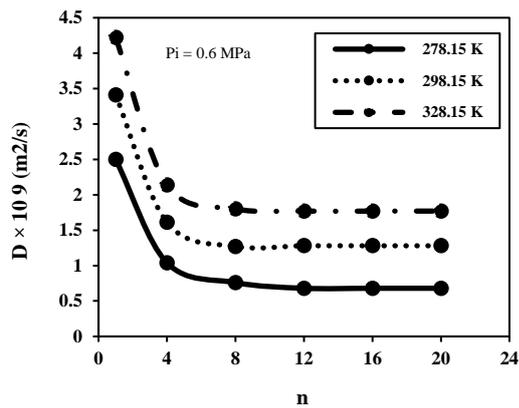


Fig. 10: Effect of considering different numbers of terms in the infinite series on the values of the molecular diffusion coefficient.

the computational time, the values of the molecular diffusion coefficients are calculated considering different number of terms in the infinite series. This work is performed for all of the nine experiments. Fig. 10 shows the results for the initial pressure of about 0.6 MPa. As can be seen, the molecular diffusion coefficient decreases up to $n=12$, but further increase of n does not change the molecular diffusion coefficient significantly. This trend is also observed in other experiments. Therefore, all the calculations in the developed model are performed considering the first twelve terms of infinite series ($N=13$) instead of $N=1$ in the initial model.

Fig. 11 shows the variation of tuned optimum diffusion coefficient and the model error according to the guessed equilibrium pressure. The minimum of the error curve corresponds to the optimum diffusion coefficient and equilibrium pressure as the output of the calculation. It is clear that a slight change in the guessed equilibrium pressure (± 0.01 MPa) will cause a considerable change in the value of diffusion coefficient (values are depicted in Fig. 11). Therefore, it is inferred that the diffusion coefficient obtained by the proposed model is very sensitive to the equilibrium pressure as well as the initial model. However, one of the advantages of the proposed model is that not only the equilibrium pressure is not required as an input datum, but also it can be calculated by the model.

In order to accurately analyse the equilibrium pressure and the time needed to attain it, the ethylene concentration profile along the liquid depth is plotted in Fig. 12 using the developed model. As can be seen in Fig. 12, the gas diffusion depth in the liquid column increases more and

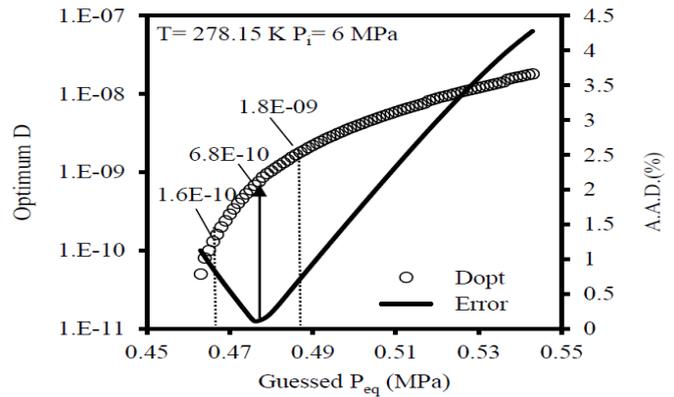


Fig. 11: Sensitivity analysis of diffusion coefficient obtained from the proposed model to the equilibrium pressure.

more as time increases. Eventually, at the time of about 28 h, the diffusing species reaches the bottom of the cell. After this time, the diffusion rate decreases so that after about 100 h, the concentration gradient still exists in the cell, and the equilibrium is not achieved. Another point which is observable in Fig. 12 is that the concentration at the interface ($x = 0.035$ m) is changing with time. As previously explained in the boundary condition, the concentration at the interface is a function of gas pressure which decreases with time.

CONCLUSIONS

In this study, mass transfer modelling on the basis of Fick's second law was performed to calculate the molecular diffusion coefficients of ethylene in NMP. The modelling results have been compared with a graphical model, named initial model, which involved some more simplifications. The required pressure decay data and also the equilibrium pressures were measured experimentally. The initial model was found to be highly sensitive to the equilibrium pressure such that a considerable change in the molecular diffusion coefficient is found as a result of an infinitesimal change in the equilibrium pressure, which may naturally occur in the experiments. Another drawback of the initial model was the neglect of the second term onwards in the infinite series. This simplification caused a remarkable error in the calculation of the molecular diffusion coefficient. In the proposed model, the equilibrium pressure was considered as a tuning parameter, and was not required to be measured in the experiment. Moreover, any number of the terms in the infinite series were considered for the calculation

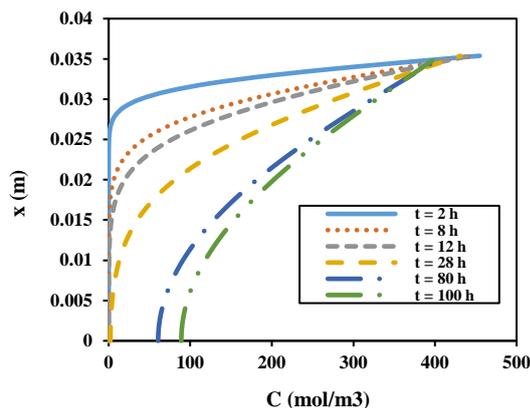


Fig. 12: Concentration profile of diffusing gas inside the liquid column.

of diffusion coefficient. With the computational time being taken into account, the first twelve terms of infinite series ($N=13$) were found to be sufficient to give the molecular diffusion coefficient with acceptable accuracy. The proposed model was organized so that the values of the molecular diffusion coefficient and also the equilibrium pressure could be adjusted. It is worth mentioning that the optimum values of the equilibrium pressure obtained from the developed model were slightly less than those measured in the experiments. Results showed that the molecular diffusion coefficient increases with increasing temperature and pressure. Moreover the molecular diffusion coefficient of the present work was found to be more sensitive to the pressure variation, than temperature. The concentration profiles at different times were drawn based on the proposed model, and as expected, the concentration at the interface decreased with increasing time. Finally, comparison of the proposed model and the initial model with Wilke-Chang model revealed that the proposed model not only poses a powerful theoretical background, but also showed a better agreement with the Wilke-Chang model.

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