Kinetic of Methane Hydrate Formation in Micro- and Nanodroplets

MEHRDAD MANTEGHIAN*, REZA DOROSTI and ABOLFAZL MOHAMMADI

Department of Chemical Engineering, Tarbiat Modares University, Tehran, Iran

*Corresponding author: Fax: +98 21 88005040; Tel: +98 21 82883333; E-mail: manteghi@modares.ac.ir

In this research, the kinetic of hydrate formation from a microdroplet or nanodroplet is investigated. The shrinking core model is used for predicting of hydrate growth on a droplet. In this model, it assumed that the nucleation was started on the outer surface of water droplet and the direction of hydrate growth is into the center of the droplet. Diffusion of the gas molecules through the gas film surrounding the droplet, diffusion through the hydrate layer and reaction with the outer surface of unreacted water is the steps of hydrate formation in shrinking core model. The reaction rate constant of methane molecules with water droplet (k) is extracted from literature. Using shrinking core model showed that, in nanodroplets and droplets smaller than 1 μm, reaction of gas molecules with water droplet is the main resistance in the hydrate formation. By increasing the size of water droplets, the resistance of diffusion through the hydrate film was increased and in droplet larger than 100 μm, the main resistance of hydrate formation was diffusion of gas molecules. By increasing the temperature, the effect of chemical reaction in hydrate formation resistances was increased.

Key Words: Nanodroplet, Microdroplet, Hydrate, Kinetic, Shrinking core model, Mass transfer, Methane.

INTRODUCTION

Gas hydrates, or clathrate hydrates, are ice-like crystalline compounds formed by the inclusion of low molecular diameter non-polar or slightly polar molecules inside cavities formed by water molecules[1]. Currently, gas hydrate technology is being widely used in the fields of storage and transportation of natural gas, seawater desalination, carbon dioxide sequestration and cold storage air-conditioning. Therefore, it is substantially important to perform studies on gas hydrate[2]. Slow formation rate of natural gas hydrate is a critical problem hindering the industrial application of this technology. One way to increase the hydrate formation rate is using of surfactants. At our previous works, we have used various surfactants for increasing the rate of dissolution and hydrate formation[3-5].

Electrospraying is a method of droplet production. Droplets, which produced by this method are highly charged, that prevents their coagulation and promotes self-dispersion. In electrospraying method the size of the droplets can be controlled to some extent by voltage and flow rate[6]. The kinetic modeling of hydrate formation so far has been developed based on a stirred tank batch, where a reactor containing water maintained at hydrate forming conditions is injected with gas and agitated to produce hydrates systems[7,8]. Recently, advanced observation and measuring methods have been adopted in the researches of hydrate formation kinetics worldwide[9-13]. Lee *et*

al.[14] studied the gas hydrate formation and decomposition of water droplets using methane-ethane and methane-propane mixtures. Ohmura *et al.*[15] reported the visual observation of the formation and growth of structure-H hydrate crystals on a water droplet. In this research, we will investigate the kinetic of hydrate formation from a micro- and nanodroplet.

EXPERIMENTAL

Fig. 1 shows the proposed mechanism of hydrate formation from a droplet surrounding by gas molecules.
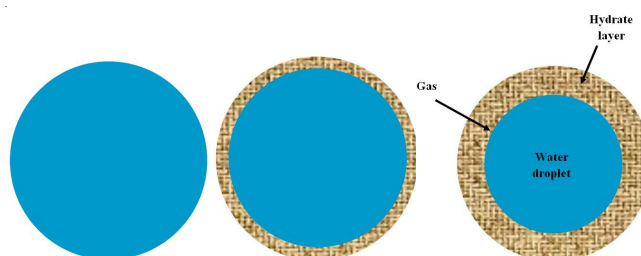

Fig. 1. Proposed mechanism of hydrate formation from a water droplet; a) Initial droplet that surrounded by gas molecules; b) A thin film of hydrate that is formed from the outer surface of initial droplet; c) Growth of hydrate layer from surface to the center of droplet

In shrinking core model, hydrate formation of a water droplet consist of three steps[16]: (1) Diffusion of the gas

molecules (A) through the gas film surrounding the droplet; (2) Diffusion of gas molecules through the hydrate layer; (3) Reaction of gas molecules with the outer surface of unreacted water.

The reaction of hydrate formation is shown in eqn. (1):

$$A(gas) + bB(water\ droplet) \rightarrow sS(hydrate) \qquad (1)$$
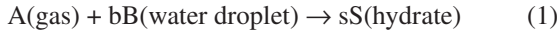
The resistance of gas film is negligible in comparison of two other resistances. Diffusion through the hydrate layer, hydrate formation reaction or combination of these two steps is the rate-controller in hydrate formation process. From the eqn. (1) it can be written:

$$dn_B = b.dn_A \qquad (2)$$

$$dn_B = d(\rho_B V / M_B) = \frac{\rho_B}{M_B} d(\frac{4}{3}\pi r_C^3) = \frac{4\pi\rho_B r_C^2}{M_B} dr_c \qquad (3)$$

where, ρ_B, M_B, V and r_C are density, molecular weight, instant volume and radius of a water droplet respectively.

If diffusion of gas A through the gas film being the rate-controller of hydrate formation process, the flux of water conversion to hydrate can obtain from eqn. (4):

$$\frac{-1}{S_{ex}}\frac{dn_B}{dt} = \frac{-1}{4\pi R^2}\frac{dn_B}{dt} = \frac{-b}{4\pi R^2}\frac{dn_A}{dt}$$
$$= bk_G(C_{Ag} - C_{As}) = bk_G C_{Ag} \qquad (4)$$

In this equation, S_{ex} is the initial surface of droplet, R is the initial radius of droplet, b is the stoichiometric coefficient in eqn. (1), k_G is the mass transfer coefficient between gas molecules and water droplet, C_{Ag} is the concentration of A in gas bulk and C_{As} is the concentration of gas A on the outer layer of hydrate (r = R). If gas film being the main resistance, we can assume that C_{As} = 0. By substituting the eqn. (3) in eqn. (4) and integrating of it:

$$t = \frac{\rho_B R}{3bk_G M_B C_{Ag}}\left[1 - \left(\frac{r_C}{R}\right)^3\right] \qquad (5)$$

If diffusion through the hydrate layer being the main resistance of the hydrate formation process, by writing the steady-state mole balance for the control volume showing in Fig. 2, eqn. (6) can be obtained as following:

$$A.N_{Ar}|_r - A.N_{Ar}|_{r+dr} = 0 \Rightarrow \frac{d}{dr}(A.N_{Ar}) = 0 \qquad (6)$$

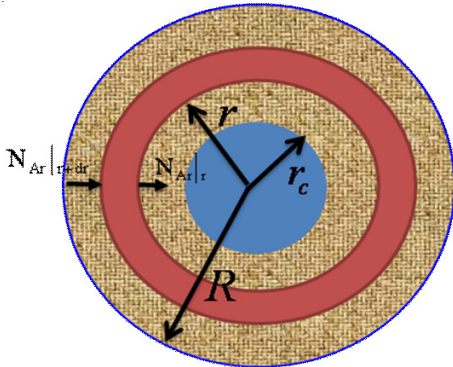That A is the surface of hydrate layer at radius r and N_{Ar} is the mole flux of gas A at radius r.

Fig. 2.　Control volume for the state that diffusion through the hydrate film is rate-controller of hydrate formation process

In this state it is assumed that the rate of diffusion through the hydrate layer in any instant is equal to the rate of reaction of A:

$$-\frac{dn_A}{dt} = 4\pi r^2.N_{Ar} = 4\pi R^2.N_{As} = 4\pi r_c^2.N_{Ac} = cte \qquad (7)$$

where, N_{Ac} and N_{As} are the mole fluxes of gas A at r_C and R respectively. Fick's law for the diffusion is given in eqn. (8):

$$N_{Ar} = D_e \frac{dC_A}{dr} \qquad (8)$$

where, D_e is the effective diffusivity of gas A in the hydrate layer. Substituting eqn. (8) in to the eqn. (7) yields:

$$-\frac{dn_A}{dt} = 4\pi r^2 D_e \frac{dC_A}{dr} = cte \qquad (9)$$

By integrating of eqn. (9) from R to r_C:

$$-\frac{dn_A}{dt}\int_R^{r_c}\frac{dr}{r^2} = 4\pi D_e \int_{C_{As}=C_{Ag}}^{C_{Ac}=0} dC_A \qquad (10)$$

Or

$$-\frac{dn_A}{dt}(\frac{1}{r_c} - \frac{1}{R}) = 4\pi D_e C_{Ag} \qquad (11)$$

By combining the eqns. (2) and (3):

$$dn_A = dn_B / b = \frac{4\pi\rho_B r_c^2}{bM_B} dr_c \qquad (12)$$

By substituting the eqn. (12) in the eqn. (11) and integrating of it, the relation of unreacted water droplet radius with time will obtain:

$$t = \frac{\rho_B R^2}{6bD_e M_B C_{Ag}}\left[1 - 3\left(\frac{r_C}{R}\right)^2 + 2\left(\frac{r_C}{R}\right)^3\right] \qquad (13)$$

If reaction of gas molecules with water droplet being the rate-controller, according to Fig. 3, it is assumed that the concentration of A in hydrate layer, gas film and gas bulk is equal:

$$C_A = C_{As} = C_{Ac} = C_{Ag} \qquad (14)$$

The reaction of hydrate formation occurs in r = r_c, so the reaction rate obtains from eqn. (15).

$$\frac{-1}{A_c}\frac{dn_A}{dt} = \frac{-1}{4\pi r_c^2}\frac{dn_A}{dt} = kC_{Ag} \qquad (15)$$

That k is the reaction rate constant.

By combining the equations (2) and (15):

$$\frac{-1}{A_c}\frac{dn_B}{dt} = \frac{-b}{A_c}\frac{dn_A}{dt} = \frac{-b}{4\pi r_c^2}\frac{dm_A}{dt} = bkC_{Ag} \qquad (16)$$

By substituting the eqn. (16) in the eqn. (12) and integrating of it:

$$t = \frac{\rho_B R}{bkM_B C_{Ag}}\left[1 - \frac{r_C}{R}\right] \qquad (17)$$

If all three steps have a high resistance for hydrate formation, the required time for reducing the radius of unreacted water droplet obtain by summing the time of three above steps:

$$t = \frac{\rho_B R}{bM_B C_{Ag}}\left\{\frac{1}{3}\frac{1}{k_G}\left[1 - \left(\frac{r_C}{R}\right)^3\right] + \frac{1}{6}\frac{R}{D_{eff}}\right.$$
$$\left.\left[1 - 3\left(\frac{r_C}{R}\right)^2 + 2\left(\frac{r_C}{R}\right)^3\right] + \frac{1}{k}\left[1 - \frac{r_C}{R}\right]\right\} \qquad (18)$$
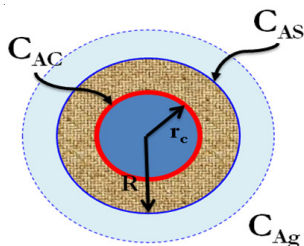
Fig. 3. Various concentrations of gas molecules for state that chemical reaction is the rate-controller of hydrate formation process

RESULTS AND DISCUSSION

Generally, the resistance of diffusion in gas film is negligible in hydrate formation process. Thus in this paper it is assumed that the main resistances of hydrate formation are diffusion in hydrate layer and reaction between gas molecules and water droplet. Bergeron *et al.*[17] presented the reaction rate constant of hydrate formation at three temperatures. The data is given in Table-1.

TABLE-1
REACTION RATE CONSTANTS FOR METHANE HYDRATE
FORMATION AT VARIOUS TEMPERATURES[17]

Average temperature (K)	275.1	277.1	279.1
Reaction rate constant ($\times 10^{-8}$ m/s)	8.3 ± 0.5	21.5 ± 3.9	61.5 ± 4.8

As respects the methane molecules forms the structure I of hydrate and assuming that the reaction is complete, the constant of b in eqn. (1) will be equal to 5.75. The required time for complete conversion of water droplet to gas hydrate (τ) can be obtained by substituting the $r_c = 0$ in eqns. (13) and (17). τ_D and τ_r represent the τ for the states that the rate-controller of hydrate formation being diffusion and reaction, respectively.

$$\tau_D = \frac{\rho_B R^2}{6 b D_e M_B C_{Ag}} \qquad (19)$$

$$\tau_r = \frac{\rho_B R}{b k M_B C_{Ag}} \qquad (20)$$

We defined the D_a as the ratio of the reaction rate constant to the effective diffusivity of gas A in hydrate film.

$$D_a = \frac{k}{D_e} \qquad (21)$$

For various values of effective diffusivity in the range of 10^{-13}-10^{-10} m²/s, the amount of D_a was calculated for three temperatures of 275.1, 277.1 and 279.1 K and was given in Table-2.

TABLE-2
VALUES OF D_a FOR THE VARIOUS EFFECTIVE DIFFUSIVITIES
IN THE RANGE OF $10^{-13} - 10^{-10}$ m²/s AND THE REACTION RATE
CONSTANTS LISTED IN TABLE-1

Average temperature (K)	275.1	277.1	279.1
D_a (m⁻¹)	8.3×10^2-8.3×10^5	21.5×10^2-21.5×10^5	61.5×10^2-61.5×10^5

According to the eqn. (21) by increasing the effective diffusivity, rate of the reaction rate constant (D_a) decreases.

To obtain the effect of droplet size on the rate-controlling mechanisms of mass transfer, the droplets with the radius of

100 nm-100 µm have been studied. Figs. 4-6 depict the amounts of τ_D and τ_r for all data of D_a that are listed Table-2. By comparison of the Figs. 4-6 (specially in the sections of C of this figures), it can be understood that increasing of the temperature at the constant pressure, droplet radius and D_a, would decrease the effect of chemical reaction on the rate-controlling of the hydrate formation. From Table-1, it can be seen that by increasing the temperature of system, the rate constant of hydrate formation reaction was increased and according to eqn. (20), increasing of k causes decrease of τ_r.
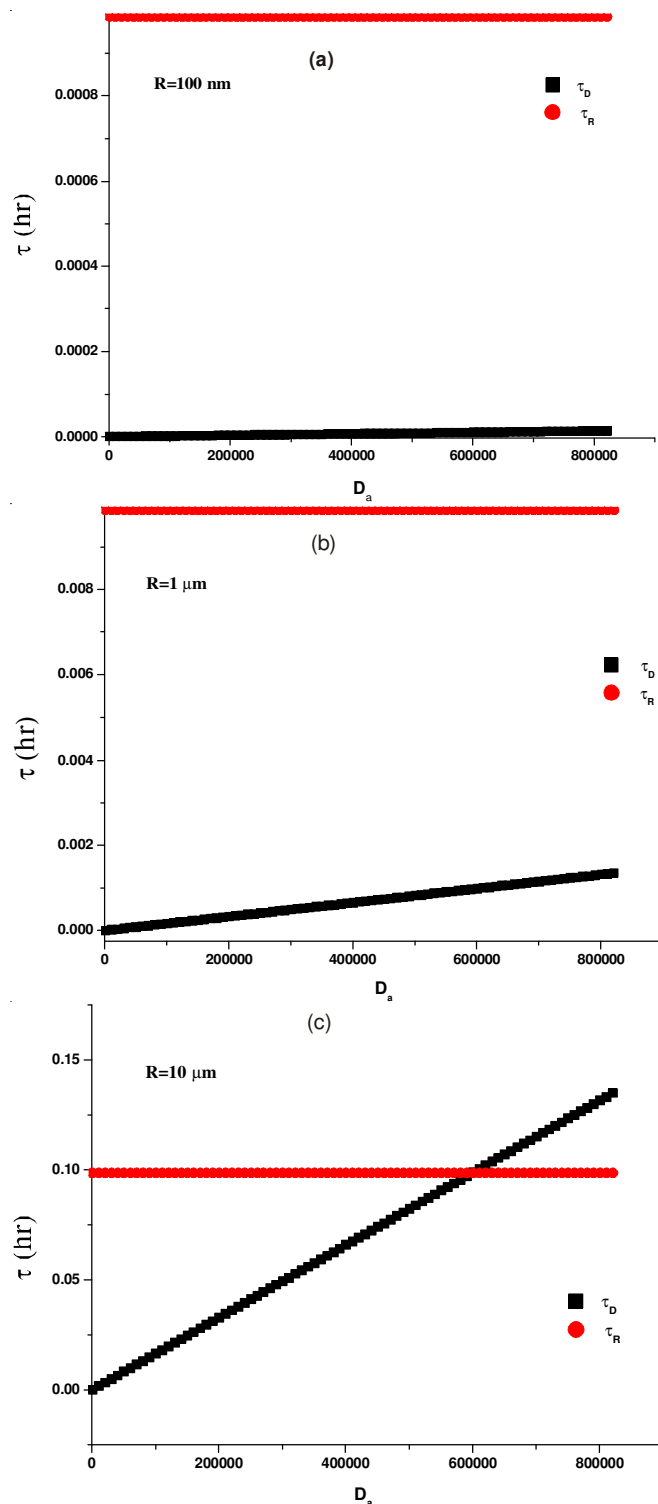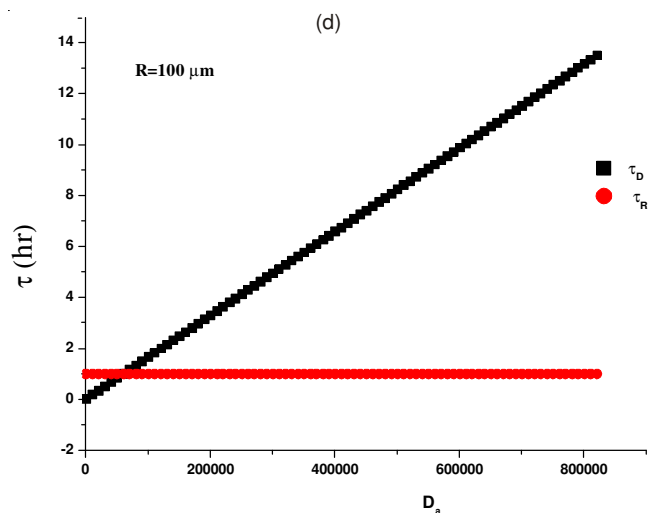
Fig. 4.   Required time (τ) for complete conversion of water droplet to hydrate at 75 bar and 275.1 K and at various D_a; a) R = 100 nm; b) R= 1 μm; c) R = 10 μm; d) R=100 μm

As can be seen in each Figs. 4-6, by increasing the initial radius of water droplet at constant temperature and pressure, both diffusion and reaction resistances was increased but increases in diffusion resistance is more than the increases in reaction resistance. For example in Fig. 4-a (T = 275.1 K and R = 100 nm), at all values of D_a the amounts of τ_r are greater than τ_D; this means that the reaction is rate-controller of hydrate formation. By increasing the initial radius of droplet to 100 μm (Fig. 4-d), the increasing amount of τ_r and τ_D at D_a = 7 × 10^5 m^{-1} was 0.986 and 11.518 h respectively. These results show that at low amounts of D_a, the chemical reaction between gas molecules and water droplet is rate-controller and at higher amounts of D_a, the diffusion of gas molecules through the hydrate layer is rate-controller of hydrate formation process. In Fig. 4-d (R = 100 μm) it is observed that only at very low amounts of D_a, the reaction is rate-controller and in wide range of D_a, the diffusion in gas layer is the controller of hydrate formation process. Generally, it can be concluded that by increasing the initial size of water droplet, the resistance of diffusion increases and in large size (R > 100 μm) of water droplet, diffusion is the rate-controller of hydrate formation. These results are confirmed by eqns. (19) and (20). In these equations $\tau_r \propto R$ and $\tau_D \propto R^2$.

Conclusion

The kinetic of hydrate formation for water droplets was modeled by using shrinking core model. The main resistances in hydrate formation process are diffusion of gas molecules in hydrate layer and reaction of gas molecules with water droplet and the resistance of gas diffusion through the gas film is
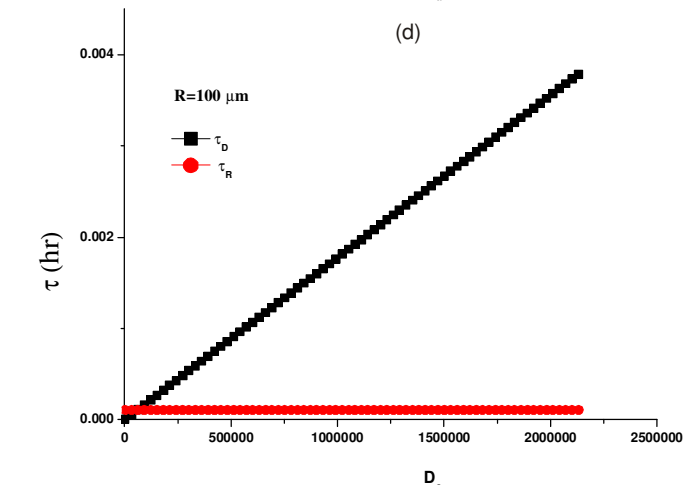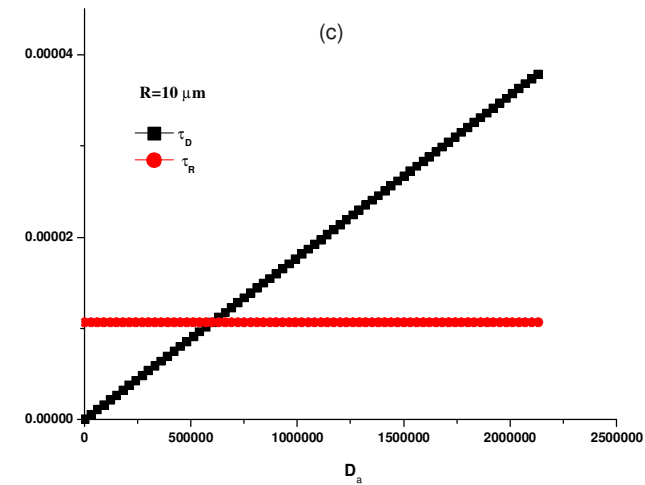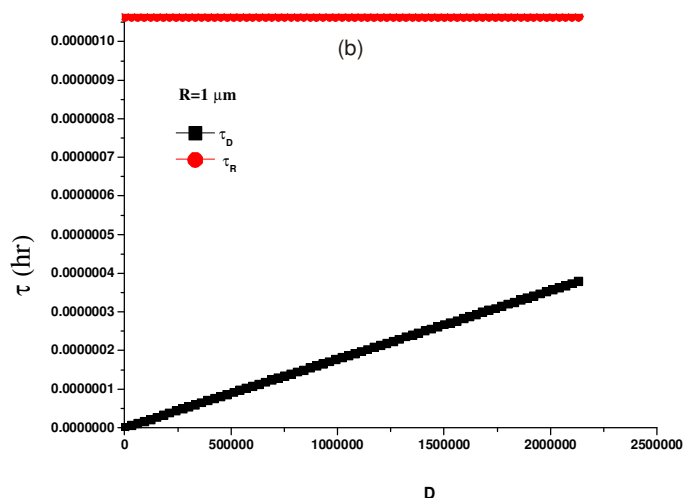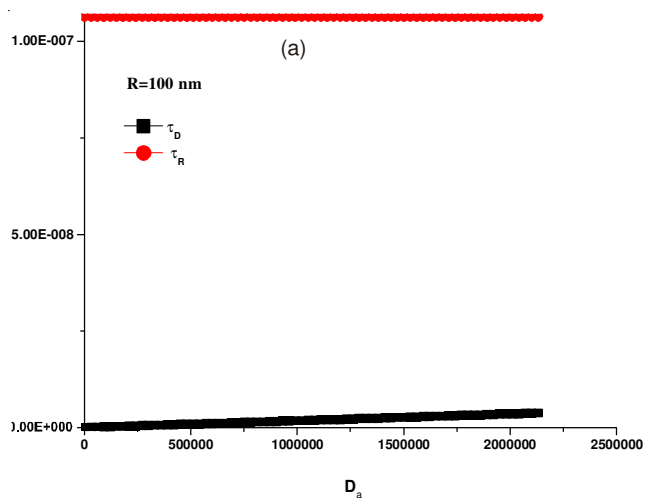

Fig. 5.   Required time (τ) for complete conversion of water droplet to hydrate at 75 bar and 277.1 K and at various ; a) R=100 nm; b) R= 1 μm; c) R=10 μm; d) R=100 μm
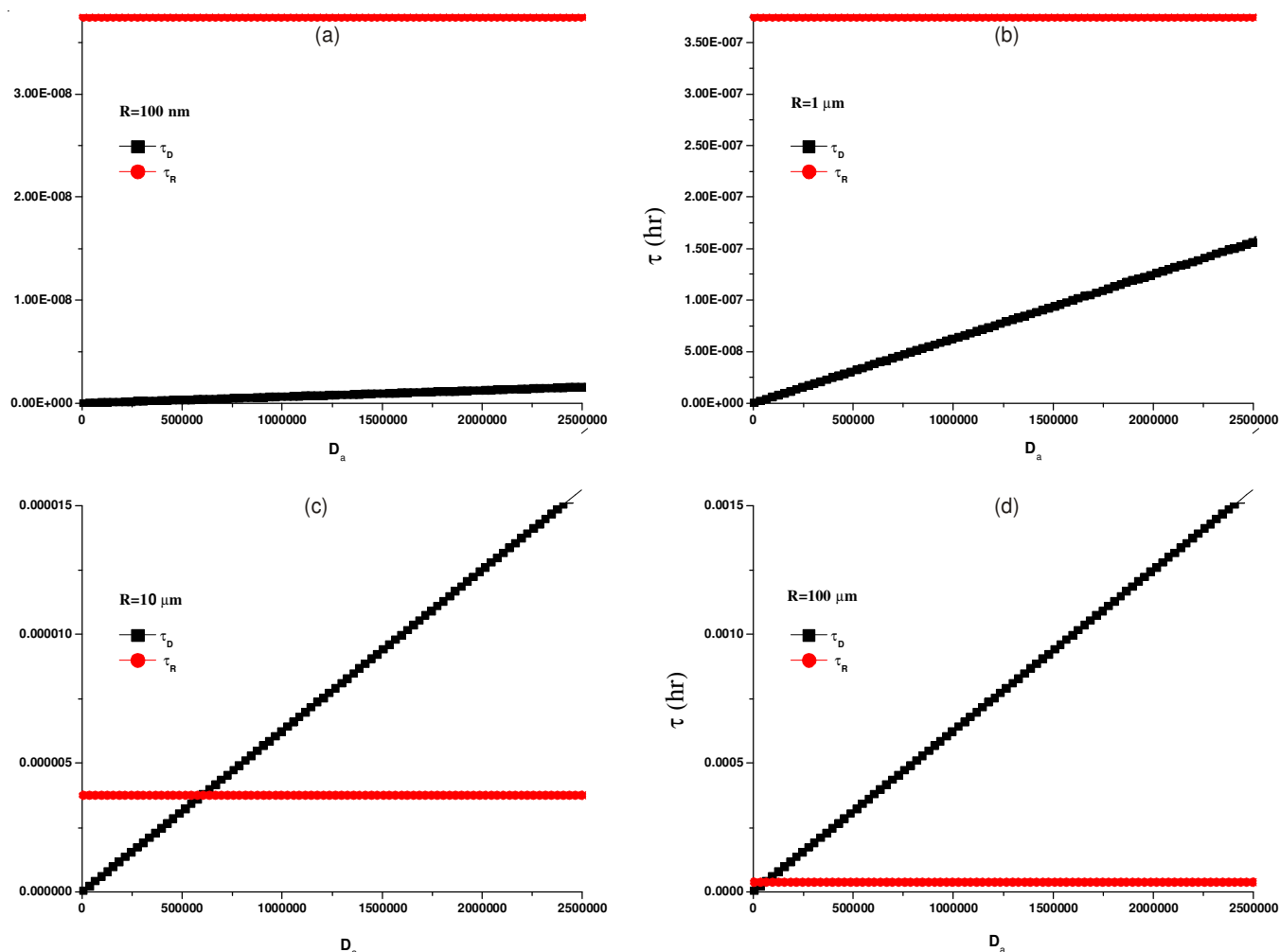
Fig. 6.   Required time (τ) for complete conversion of water droplet to hydrate at 75 bar and 279.1 K and at various D_a; a) R = 100 nm; b) R = 1 μm; c) R = 10 μm; d) R = 100 μm

negligible. The reaction rate constants of hydrate formation process were extracted from literature. For a wide range of effective diffusivity, the reaction and diffusion resistances were compared. By increasing the temperature, the effect of chemical reaction on the rate-controlling of hydrate formation increases. In the small water droplets (R<1 μm), the rate-controller of process is chemical reaction and in large droplets (R > 100 μm) diffusion of gas molecules in hydrate layer is the rate-controller of hydrate formation process.

ACKNOWLEDGEMENTS

REFERENCES

1. E.D. Sloan, Clathrate Hydrates of Natural Gases, Marcel Dekker, New York, edn. 2 (1998).
2. S.S. Fan, Technology in the Storage and Transport of Natural Gas Hydrate. Beijing: Chemical Industry Press (2005).
3. a) H. Ganji, M. Manteghian and H.R. Mofrad, *Fuel Proces. Technol.* **88**, 891 (2007); b) H. Ganji, M. Manteghian, K.S. Zadeh, M.R. Omidkhah and H.R. Mofrad, *Fuel*, **86**, 434 (2007).
4. a) A. Mohammadi, M. Manteghian and M. Mirzaei, *Chem. Eng. Res. Des.*, **89**, 421 (2011); b) A. Mohammadi, M. Manteghian, S.M. Hoseini Nasab and S.M. Mousavi, *Petroleum Sci. Technol.*, (Accepted); c) A. Mohammadi,

M. Manteghian and S.M. Mousavi, *Petroleum Sci. Technol.*, (Accepted).
5. M. Manteghian, M. Azimi and J. Towfighi, (Coomunicated) (2011).
6. A. Jaworek, *Powder Technol.*, **176**, 18 (2007).
7. a) P. Englezos, N. Kalogerakis, P.D. Dholabhai and P.R. Bishnoi, *Chem. Eng. Sci.*, **42**, 2647 (1987); b) P. Englezos, N. Kalogerakis, P.D. Dholabhai and P.R. Bishnoi, *Chem. Eng. Sci.*, **42**, 2659 (1987);
8. P. Skovborg, H.J. Ng, P. Rasmussen and U. Mohn, *Chem. Eng. Sci.*, **48**, 445 (1993).
9. D.L. Zhong, D.P. Liu and Z.M. Wu, Modeling of Natural Gas Hydrate Formation on a Suspended Water Droplet, Proceedings of the 6th International Conference on Gas Hydrates (ICGH), Vancouver, British Columbia, CANADA (2008).
10. N. Gnanendran and R. Amin, *Chem. Eng. Sci.*, **59**, 3849 (2004).
11. M. Sugaya and Y.H. Mori, *Chem. Eng. Sci.*, **51**, 3505 (1996).
12. C.Y. Sun, G.J. Chen and T.M. Guo, *Science in China (Series B)*, **46**, 487 (2003).
13. M. Eaton, D. Mahajan and R. Flood, **56**, 101 (2007).
14. J.D. Lee, R. Susito and P. Englezos, *Chem. Eng. Sci.*, **60**, 4203 (2005).
15. R. Ohmura, M. Sadatoshi, I. Sinya, T. Ebinuma and H. Narita, Formation and Growth of Structure-H Hydrate Crystals on a Water Drop in Contact with Methane Gas and Large-molecule Guest-substance Liquid, Proceedings of the 5th International Conference on Gas Hydrate, Norway (2005).
16. O. Levenspiel, Chemical Reaction Engineering, Wiley, edn. 3 (1998).
17. S. Bergeron, J.G. Beltrán P. Servio, *Fuel*, **89**, 294 (2010).