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Microwave Selective Heating Assisted Distillation Process of Two Components System

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Microwave is widely used in heating process both at home and in the industry sector, due to its advantages, such as capacity to rapidly transmit heat, penetration power, convenience *etc*. The interest in microwave heating has been witnessed in the last 40 years by an increasing number of new applications and theoretical studies, but seldom investigation is focused on its selective heating based on dielectric constant of heated substance. In this paper, two-component miscible system is investigated in microwave field with or without vacuum, some parameters such as temperature rise, heat transfer, evaporation volume and other factors were analyzed. Microwave select heating process is preliminary understood and its potential application in molecular distillation is proved.

Keywords: Microwave, Selective heating, Molecular distillation.

INTRODUCTION

Microwave technique is widely used in social life and many industrial productions. Microwaves have wavelengths ranging from 1-1000 mm and frequency ranging from 3.3-300 GHz. Based on the dielectric constant of the material, the microwave gives overall heating within it penetrate scope. Compared to traditional heating, microwave heating has advantages such as short heating time, uniform temperature distribution and high energy efficiency.

The principle of microwave heating in the microwave field is that a polar molecule under the action of high intense friction caused by the rotation, so that the material was heated and the temperature was increased rapidly. Based on the advantages of microwave heating, it is gradually replacing the traditional heating methods in many producing process. Adoption of microwave in extraction of active ingredients can greatly shorten the reaction time[1,2]. Microwave technology can also be used in drying process and obtained higher quality products, because conventional heating method can lead to part overheating[3]. Another advantage can be found in microwave assist chemical reaction process, microwave technology can increase the reaction rate, improve product yield and purity[4,5]. In separation and purification, solvent free microwave extraction has higher efficiency than common steam distillation and extraction time can be shortened by the 180 min to only 15 min[6,7].

In microwave assisted herbal extraction process, studies have shown that microwave heating has certain heating selectivity in addition to shorten the extraction time. The heating selectivity is helpful to promote separation process of active ingredient from the cells and penetration process of active ingredient over the cell wall into the extraction solvent[8]. Research has shown that liquid water exist mainly in the form of clusters because of hydrogen bonds[9]. And a single water molecule breakdown from water clusters is a critical step that restricting the evaporation of water molecules. Microwave treatment can destroy hydrogen bonds and change the structure of water molecule cluster for at least 7 h. Therefore, the microwave heating of liquid water can not only increasing heating rate, but also produce non-thermal effects and changes structural state of water molecule clusters. Microwave can provide rapid temperature increasing, which compensates the temperature decrease caused by evaporation and temperature polarization. Temperature compensation could be achieved more efficiently by microwave for its characteristics such as rapid and uniform, compared with conventional heating.

Although microwave technology is widely used in many ways, but only short heating time and uniform temperature distribution have often been concentrated. Few researches were focused on the heating selectivity which based on the dielectric constant. Our previous studies have been carried out in two immiscible phases, aqueous phase and oleic phase. The result shows that aqueous phase and oleic phase has different temperature rising rate due to different dielectric constant. The water molecules can be selectively evaporated while temperature of oleic phase is low, because of the smaller heat transfer surface area between two phases[10]. Based on the result of it, immiscible solution can be seemed as that one kind of molecules homogeneous suspended in another kind of molecules. The main difference with immiscible solution is that heat transfer surface become larger. In this paper, investigation of microwave selective heating for the immiscible solution is carried out.

Theory analysis: Molecular distillation is different from ordinary distillation. The main difference is that molecular distillation is based on the mean free path of component in mixed solution. The mean free path λ is defined by the following relation, derived from the molecular thermodynamic theory[11]:

$$\lambda = \frac{K \cdot T}{\sqrt{2} \cdot \pi \cdot d^2 \cdot P} = \frac{R \cdot T}{\sqrt{2} \cdot \pi \cdot d^2 \cdot P \cdot N_p} \quad (1)$$

In addition to the mean free path λ, the rate of molecular distillation G and molecular distillation separation factor ε is the main parameters of molecular distillation process. Theoretical molecular distillation rate G for pure substances can be defined by eqn. (2), derived from the Langmuir-Knudsen evaporation model analysis.

$$G = P_0 \cdot x \cdot [\frac{1}{2\pi \cdot M \cdot R \cdot T_s}]^{\gamma} \quad (2)$$

Molecular distillation is a non-equilibrium separation process. Its separation factor is the ratio of molecular distillation molar rate of two components.

$$\varepsilon = \frac{y_A \cdot x_B}{y_B \cdot x_A} = \frac{G_A \cdot M_B}{G_B \cdot M_A} \quad (3)$$

Combined with eqns. (2 and 3) can be re-written for molecular distillation separation factor, as eqn. (4)

$$\varepsilon = \frac{P_A^0}{P_B^0} \times \sqrt{\frac{M_B}{M_A}} \quad (4)$$

As a result, molecular distillation separation factor increased $(M_B/M_A)^{0.5}$ times when compared with ordinary distillation. Based on microwave theory, heating rate of substance in microwave field can be expressed as eqn. (5).

$$\frac{T - T_0}{t} = \frac{0.566 \cdot 10^{-10} \cdot \varepsilon'_{eff} \cdot f \cdot E^2}{\rho \cdot C_P} \quad (5)$$

As shown in eqn. (5), temperature rise rate of condensed substance in the microwave field not only depending on the nature of the microwave field (electric field intensity E, microwave frequency f, reaction time t), but also on the nature of the substance (density ρ, specific heat capacity Cp). In two-component molecular distillation process, component A and B, the ratio of the mean free path can be expressed as eqn. (6) when only reduced pressure is executed.

$$\frac{\lambda_A}{\lambda_B} = \frac{\dfrac{K \cdot T}{\sqrt{2} \cdot \pi \cdot d_A^2 \cdot P}}{\dfrac{K \cdot T}{2 \cdot \pi \cdot d_B^2 \cdot P}} = (\frac{d_B}{d_A})^2 \quad (6)$$

Component A and B have different microwave absorption ability because of the different dielectric constant that can lead to different instantaneous temperature rise rate. Therefore, it results in mean free path ratio changes of component A and B on the surface. It can be described by eqn. (7), where ΔT_A and ΔT_B can be calculated by eqn. (5).

$$\frac{\lambda_A}{\lambda_B} = \frac{\dfrac{K \cdot (T_0 + \Delta T_A)}{\sqrt{2} \cdot \pi \cdot d_A^2 \cdot P}}{\dfrac{K \cdot (T_0 + \Delta T_B)}{2 \cdot \pi \cdot d_B^2 \cdot P}} = \frac{T_0 + \Delta T_A}{T_0 + \Delta T_B} \times (\frac{d_B}{d_A})^2 \quad (7)$$

In the microwave field, different temperature rising effect of component A and B can lead to different evaporation rate. As described in eqn. (8), when ΔT increases, molecular mass evaporation rate G increases too. Thus, the evaporation rate of component is also faster.

$$G = P_{0,(T+\Delta T)} \cdot [\frac{M}{2\pi \cdot R \cdot (T_s + \Delta T)}]^{\gamma} \quad (8)$$

Different temperature rising effect on mixed solution surface can also lead to the rising of molecular distillation separation factor. When microwave field is used for molecular distillation, the molecular distillation separation factor starts to follow the route described by eqn. (9).

$$\varepsilon = \frac{P^0_{A,(T_0+\Delta T_A)}}{P^0_{B,(T_0+\Delta T_B)}} \times \sqrt{\frac{M_B}{M_A}} \quad (9)$$

As described in eqn. (9), increasing of ΔT_A and ΔT_B can lead to saturated vapor pressure rising of component A and B. However, light component has the higher microwave absorption ability than heavy component. Temperature rising of light component is more obviously than heavy component. Therefore, saturated vapor pressure of light component is greater, causing separation factor between A and B component increased. Therefore, molecular distillation processes selectively accelerated by the microwave field radiation can be proved through the temperature rising difference of two component caused by microwave field radiation.

EXPERIMENTAL

The reagents used in the experiments were of analytical grade. Microwave oven G7020II CTL-2 Galanz and infrared thermometer DT8000 were used for heating and detection.

General procedure: Mixed solution of different concentration was pipetted into a glass container with liquid layer thickness about 0.4 mm. Then solution quality and initial temperature were recorded. Solution temperature and quality loss were recorded every 3 sec during microwave heating process with 700 W power. Every trial was done three times.

Detection method: Abbe refractometer was used for determination of component changes after heating. Changes of water are chosen as an indirect parameter for evaluation of microwave selective heating ability. Volume changes of water before and after heating were calculated according to eqn. (10). In equations, c_1 is initial concentration while c_2 is concentration after heating. m_1 and m_2 are total quality of solution before and after heating. ρ_1 and ρ_2 are density of water and glycerol, respectively.

$$\Delta V_1 = \frac{\rho_2 \cdot c_1 \cdot v - \rho_2 \cdot c_2 \cdot v + c_2 \cdot \Delta m}{\rho_2 - \rho_2 c_2 + \rho_1 \cdot c_2} \quad (10)$$

While, $\Delta m = m_1 - m_2$.

RESULTS AND DISCUSSION

Heat transfer of two immiscible phases with microwave heating: As shown in Fig. 1, when heating in microwave field, temperature increasing of pure water and pure oleic acid against time is approximately running in linear curve, named line 1 and line 4, respectively. When two immiscible liquids, oleic acid and water, was heating in the microwave field, temperature increasing rate of the water is reduced while rate of oleic acid is slightly increased. When the microwave field effect was lasts 15 sec, water was boiling, the relative interfacial area between the water and oleic acid increases suddenly, causing the rapid rise of the temperature of the oleic acid[10]. Inspired by this result, it can be predicted that miscible solution can be seen as many insoluble solute suspended in another solvent. The main difference is that interfacial area become bigger in miscible solution than that in two-phase solution.

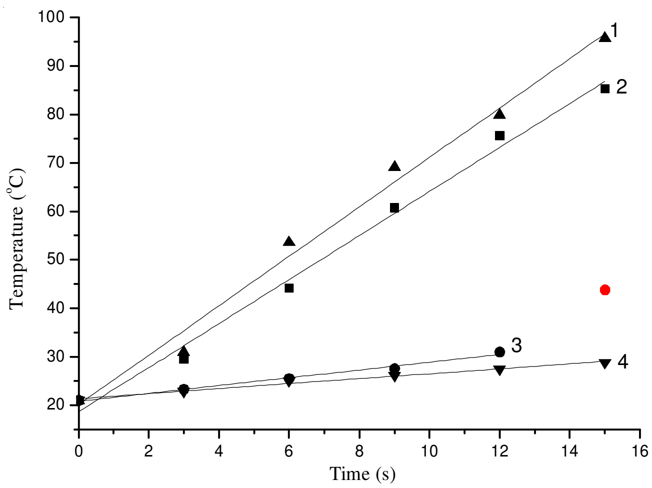

Fig. 1. Temperature changes of two-phase system with microwave heating

Factor correlation analysis of glycerol/water during microwave heating process: In order to investigate the selective heating of microwave in miscible solution, glycerol/water solution was chosen and factor correlation analysis was carried out by SPSS software. As shown in Table-1, heating time is significantly correlated with quality, volume of water and glycerol and temperature, while temperature is significantly correlated with all relevant parameters. Heating time and temperature showed a strong positive correlation. Final ratio was significant correlated temperature and initial ratio, indicating different components have different heating status in the heating process due to the different dielectric constant, that lead to the change of final ratio. In glycerol/water solution, boiling point of water is lower than that of glycerol. Changes in the volume and quality of the water are more closely related with temperature. As shown in Table-1, correlation value of heating time and water volume is 0.819 at the 0.01 level while that of heating time and glycerol volume is 0.371 at the 0.05 level. Heating time can be seen as the main control variable and it is the higher correlated with water volume. The change of water volume is large when temperature is rising, both of them showed a positive correlation. Therefore, water can be selected as indirect reference when component ratio change was investigated. At last, change of water was studied for proving the auxiliary effect of selectivity of microwave heating in the distillation.

Effect of microwave heating on glycerol/water miscible solution with different proportions: The temperature rising curve of the solutions were significantly different when glycerol was mixed with water in different proportions. As shown in Fig. 2, when water concentration is 100 and 80 %, temperature of the solution will not change any more while microwave heating time for 11s. Subsequent microwave heating process was mainly lead to evaporation of water. When water was reduced by increasing the proportion of glycerol in the system, the temperature of glycerol/water miscible system is increased. Because the boiling point of the mixture is controlled by lower boiling point, there is a corresponding longer evaporation time when a large proportion of water in the mixture. There is platform stage appear in solution with water concentration 100 and 80 % (Fig. 2). The duration of platform stage was gradually shortened while proportion of glycerol was increasing. Thus, platform stage exist from 9 to 15 s and from 18 to 24 s when water concentration 60 %. It also appeared when water concentration 40 and 20 %, 12-15 s and 24-27 s for 40 %, 15-18 and 21-24 s for 20 %, respectively. This kind of platform phenomenon indicating that heat transfer occurs between glycerol and water. Due to the higher boiling point of the glycerol molecule, glycerol was transfer heat to water and lead to water molecules evaporating. As a result, the temperature of mixed system remains substantially constant within certain limits.

Heat-transfer in glycerol/water miscible solution with different proportions: There are two main factors of heat transfer process, one of which is the temperature difference

TABLE-1
PEARSON CORRELATION ANALYSIS OF GLYCEROL/WATER MIXED SYSTEM

	Heating time	Initial ratio	Final ratio	Quality	Water volume	Glycerol volume	Temperature
Heating time	1.000	0.000	-0.212	0.856**	0.819**	0.371*	0.739**
Initial ratio	0.000	1.000	0.944**	0.206	0.266	-0.189	-0.441**
Final ratio	-0.212	0.944**	1.000	0.020	0.076	-0.167	-0.646**
Quality	0.856**	0.206	0.020	1.000	0.991**	0.025	0.439**
Water volume	0.819**	0.266	0.076	0.991**	1.000	-0.099	0.373*
Glycerol volume	0.371*	-0.189	-0.167	0.025	-0.099	1.000	0.401*
Temperature	0.739**	-0.441**	-0.646**	0.439**	0.373*	0.401*	1.000

**.Correlation is significant at the 0.01 level; *Correlation is significant at the 0.05 level

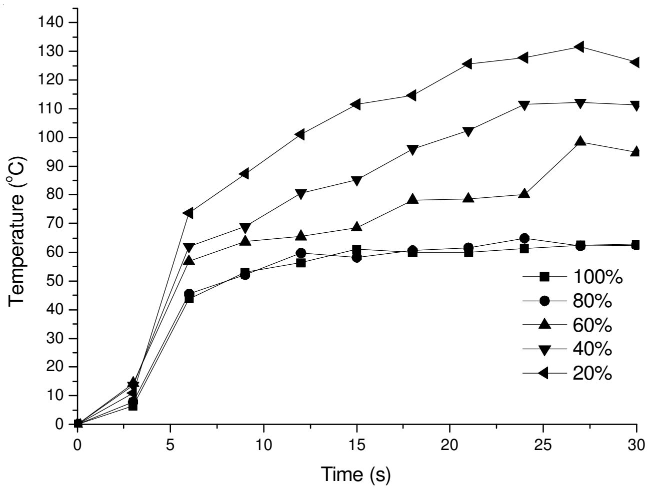

Fig. 2. Temperature rising curves of glycerol/water miscible solution with different proportions

and the second is the size of the heat transfer surface. In microwave field, molecules absorb the energy of microwave, causing rotation of itself and friction with the surrounding molecules. In addition to the rising temperatures, molecular structure can be maintained more than 7 h after the change[12]. According to this, we assume that glycerol/water miscible system is composed of two kind of rigid molecule ball. When the amount of glycerol molecules is greater than water molecules, it can be considered that all glycerol molecules are surrounded by water molecules. Then the heat transfer area is the surface area of the all glycerol molecules. When the amount of glycerol molecules is less than water molecules, heat transfer area is decided by the surface area of the all water molecules. As shown in Fig. 3, heat transfer area depends on smaller proportion one in a mixed solution. Thus, the heat transfer area can be achieved by changing the proportional relationship between the two components.

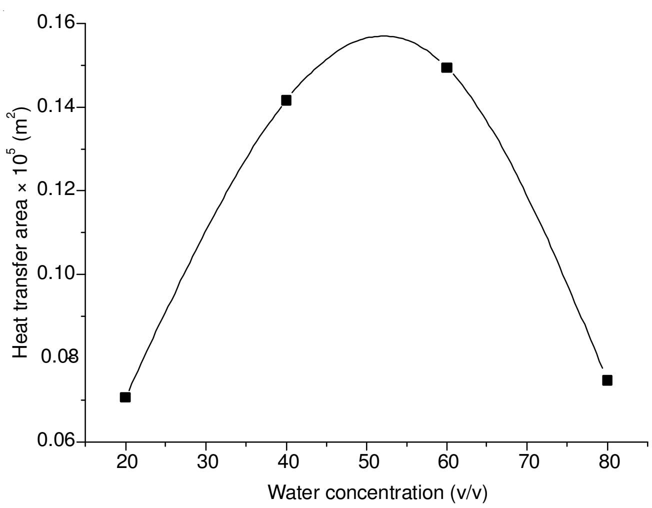

Fig. 3. Contact areas between glycerol and water in miscible solution with different proportions

For the transfer of the two components, the boiling point of the two components will be reduced in the vacuum condition. Therefore, boiling point reducing of the light component is to be a constraint for temperature rising of the whole solution. As a result, the temperature difference between the two components is lower in vacuum than that in atmospheric condition. Lower temperature difference is helpful to reduce the heat transfer phenomena. For this reason, the effect of microwave heating can be investigated by aqueous solutions of different concentrations in vacuum condition and normal pressure condition. As shown in Fig. 4, in any concentrations, the volume change rate of the aqueous solution under vacuum conditions is higher than that in normal pressure condition. Volume change rate of 80 % aqueous solution is smaller than other concentrations. Water volume change rate is increased by the decreasing of water proportion. In normal pressure condition, water volume change rate is decreased by the decreasing of water concentration while water proportion lower than 40 %. In vacuum, water volume change rate is also decreased by the decreasing of water concentration while water proportion lower than 50 %. These variations may have a significant relationship with the heat transfer area of glycerol and water.

Evaporation of water in the system was mainly associated with the absorption of microwave energy. At the same time, glycerol was also absorbing energy from microwave and improving its own temperature. Because of higher boiling point, the glycerol is difficult to evaporate but exist as a second heating source to enhance evaporation of water. Fig. 5 showed that when water concentration is 40 and 60 %, there was a larger heat transfer area. In microwave field, water molecules absorb more heat because of its higher dielectric constant. Then water transfer heat to glycerol in instantaneous by large heat transfer area and eliminate the difference of temperature. When the temperature reaches the boiling point of water, evaporation of water molecules occurs and the temperature will not increase. Glycerol will continue to absorb microwave energy because it has a higher boiling point. As a result, water will be in an overheating state and accelerate the evaporation process. In this stage, the number of glycerol determines the efficiency of the evaporation process. So the evaporation efficiency of 20 % glycerol solution is significantly low when compared to the other concentration. In the case of 80 % glycerol, a large number of binding water molecules was formed due to the existence of a large number of glycerol. Binding water is difficult to evaporate even if the temperature of the system is high.

Conclusion

Compared to conventional thermal conduction heating, microwave heating can lead to instantaneous temperature difference of the different heated substance. The temperature difference allows rapid separation of light components under high vacuum conditions. As a result, evaporation of light component can reduce the area of heat transfer surface. Separation efficiency of traditional molecular distillation can only be achieved by decreasing the pressure persistently. Microwave field effect can reduce the dependence at certain level on vacuum.

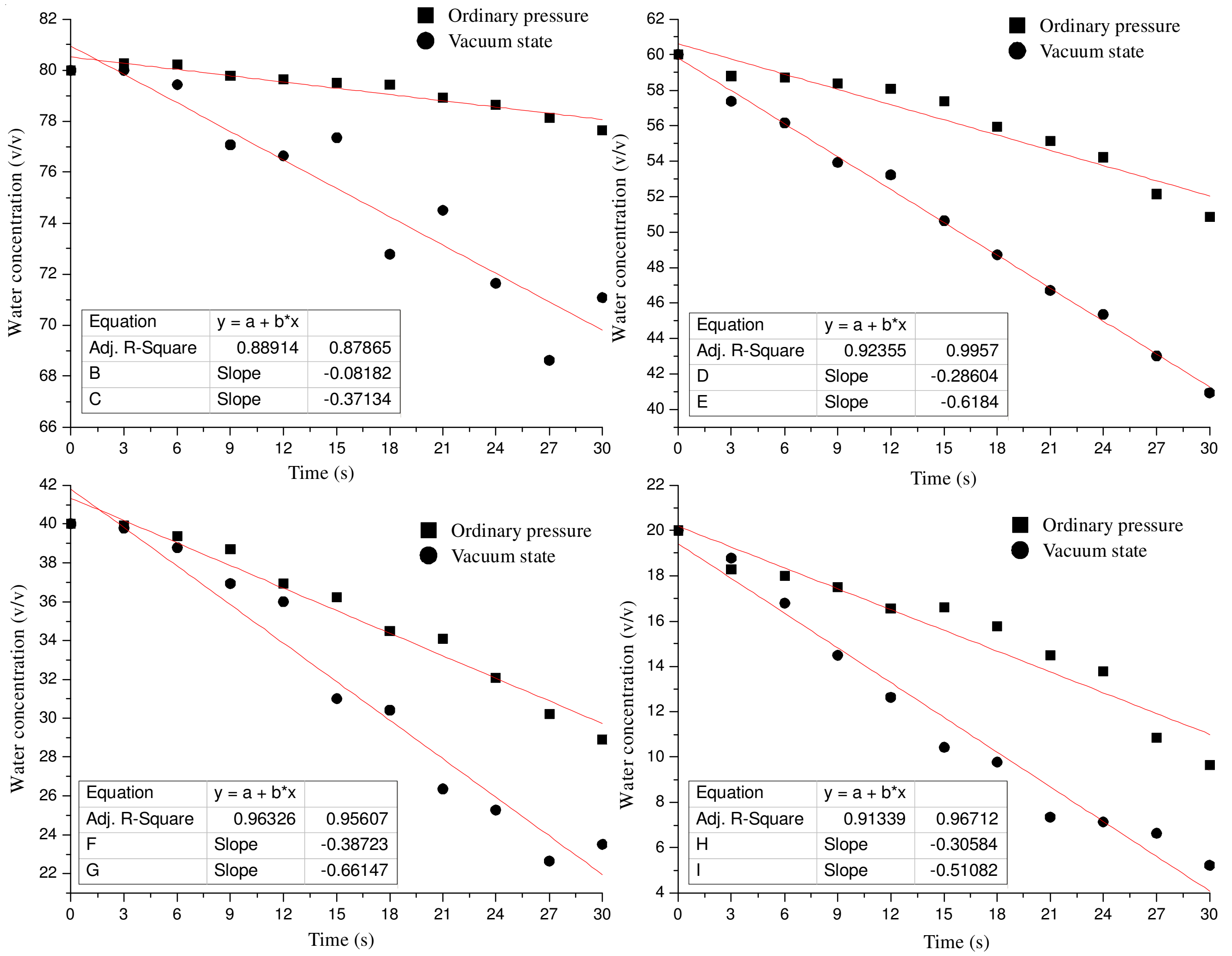

Fig. 4. Changes of water concentration in ordinary pressure and vacuum state

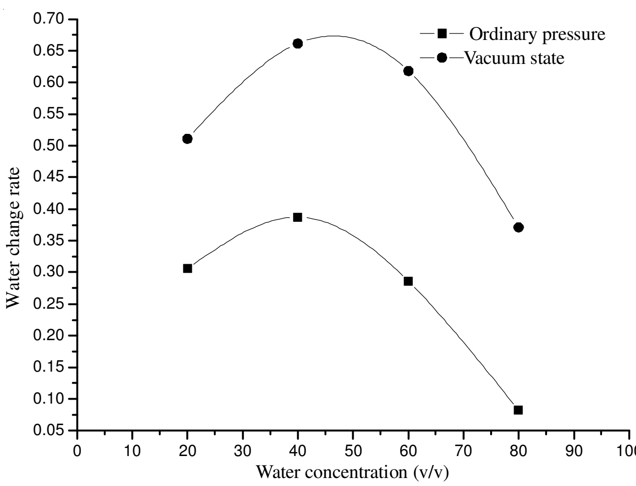

Fig. 5. Water change rate in ordinary pressure and vacuum state

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REFERENCES

1. Y. Mao, Y. Li and N. Yao, *J. Pharm. Biomed. Anal.*, **45**, 510 (2007).
2. K. Robards, *J. Chromatogr. A*, **1000**, 657 (2003).
3. S. Kocakusak, H.J. Köroglu and R. Tolun, *Chem. Eng. Process.*, **37**, 197 (1998).
4. S. Caddick, *Tetrahedron*, **51**, 10403 (1995).
5. M.A. Surati, S. Jauhari and K.R. Desai, *Arch. Appl. Sci. Res.*, **4**, 645 (2012).
6. M.E. Lucchesi, F. Chemat and J. Smadja, *J. Chromatogr. A*, **1043**, 323 (2004).
7. M.E. Lucchesi, J. Smadja, S. Bradshaw, W. Louw and F. Chemat, *J. Food Eng.*, **79**, 1079 (2007).
8. G.Z. Han, D.M. Chen, P.S. Guo and S.X. Li, *J. South China Univ. Technol. (Nat. Sci. Ed.)*, **35**, 52 (2007).
9. E.S. Kryachko, *Chem. Phys. Lett.*, **314**, 353 (1999).
10. J.Y. Xing, X.L. Song, B. Bai, S.K. Lu and H.P. Liu, *Appl. Mech. Mater.*, **448**, 3005 (2013).
11. J. Lutišan and J. Cvengroš, *Chem. Eng. J.*, **56**, 39 (1995).
12. R. Roy, M.L. Rao, S. Sedlmayr and J. Kanzius, *Curr. Sci.*, **98**, 1500 (2010).