

Experimental Study on Removal of H₂S using MDEA Solution in Microchannel

Huali Ji^{1,a}, Yanhong Zhang^{2,b}, Chenwen Wei^{3,c} and Hualin Wang^{4,d}

^{1,2,3,4}State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, China

^ajihuali700128@163.com, ^bzhyh75@ecust.edu.cn, ^cwcw_001@163.com, ^dsamwhl@163.com

Keywords: microfluidics, methyldiethanolamine, hydrogen sulfide, devulcanization

Abstract. Hydrogen sulfide is highly toxic and corrosive component of natural gas that must be removed before natural gas is used in industrial applications. Currently, absorption methods using aqueous solutions of methyl diethanolamine are most commonly employed to remove hydrogen sulfide from natural gas feedstocks. A process analysis of H₂S absorption in a microchannel is explored in this work. The results indicate that the bubbles formed at the gas-liquid interface are not consistent in size. The gas bubbles become significantly smaller in volume within 2 seconds of gas flow. There is a noticeable difference in the rate of change in bubble volume for solutions with 20 vol% and 40 vol% MDEA solution. There is also a 3.8% - 5.3% volume change within 0.6 s when 60 vol%, 80 vol%, and 100 vol% solutions of MDEA are used. From these experiments, the overall mass transfer coefficient for H₂S was calculated and it was found that the overall mass transfer coefficients $k_L a$ increases with increasing MDEA content.

Introduction

Natural gas is an abundant, inexpensive and almost non-contaminant source of energy that is widely utilized in domestic and industrial applications. Methane (CH₄) accounts for more than 90% of natural gas. Ethane (C₂H₆), propane (C₃H₈) and butane (C₄H₁₀) are other common components of natural gas. Undesirable impurities such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S) can be present in natural gas and can lead to operational difficulties, economic losses, and environmental pollution. These contaminants can cause the leakage of toxic gases, unpleasant odours and the reduction of feed quality to downstream industries [1]. Therefore, it is essential to remove these acid gases from the natural gas stream through a sweetening process. Currently, these unwanted gases are removed by absorption into physical or chemical solvents, absorption onto activated carbon, cryogenic distillation, or separation with solid and liquid membranes[2,3]. Gas-liquid absorption methods that use aqueous solutions of alkanolamines are extensively used to remove CO₂ and H₂S from gaseous streams in the natural-gas, oil-refining, petroleum and synthetic-ammonia industries[4]. Primary, secondary, and tertiary amines such as monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA), respectively, are the alkanolamine solvents used. Since the 1980s, the diisopropanolamine (DIPA) and MDEA desulfurization solvents have been utilized in industrial applications due to their selective absorption abilities [5,6,7]. MDEA in particular can be used at high concentrations, has high sour gas loading, low corrosion, and has a strong ability to resist degradation, a high selectivity for H₂S.

Alcohol amine desulfurization and decarbonization technologies have been extensively studied. For example, *Komati et al.*[8] have studied the absorption process in CO₂/MDEA solution by using nanoferrofluid in a wetted-wall column. Their results show an overall enhancement in mass transfer compared to the absence of ferrofluids with a mass transfer coefficient of 92.8% for a 50% volume fraction of the fluid (solid magnetite volume fraction of about 0.39%). *Yoosuka et al.*[9] have developed an inexpensive fumed silica that has been modified by amines and has the ability to remove both CO₂ and H₂S. They have also tested different amines to achieve the highest CO₂ and H₂S sorption capacities. *Taheria et al.*[10] have studied the simultaneous removal of CO₂ and H₂S from natural gas through DEA-based nanofluids that contain SiO₂ and Al₂O₃ nanoparticles in a wetted-wall absorber.

They report a 40% improvement of CO₂ absorption using 0.05 wt.% of SiO₂/DEA nanofluids with a deterioration in H₂S absorption. *Borhani et al.* [11] have developed a rate-based model of an absorber packed column for the simultaneous absorption of many acid gases into a methyldiethanolamine (MDEA) aqueous solution. Their parametric study showed that the concentration of the acid gases in the sweet gas stream increased as the specific surface area of packing decreased. The peak of the selectivity factor decreased with increasing mole ratio of CO₂/H₂S in the gas feed along the packed column.

During a sweetening process, CO₂ must compete with H₂S to be absorbed by the MDEA solution. At the same time, the presence of CO₂ increases the selectivity of H₂S absorption and decreases the H₂S absolute efficiency [12]. Currently, there are no studies on the reactivity between H₂S and amine. The reaction mechanisms of alcohol amine compounds and acidic gases have been elucidated as many of these reactions are used in industry. In general, when compared to homogeneous reactions, these reactions are difficult to conduct because the efficiency of interaction and the mass transfer between the different phases are low. To overcome these difficulties and thereby accelerate these reactions, systems with high interfacial areas could be of use.

Microfluidics is the science and technology of systems that process small (10⁻⁹ to 10⁻¹⁸ litres) amounts of fluid [13]. Work in this field has led to the highly-controlled dispersion of gases into liquids, from isolated bubbles to organized microfoams. There are many potential technological applications for these types of dispersions, such as novel materials, scaffolds for tissue engineering, and enhanced oil recovery. More fundamentally, microfluidics allows for the investigation of the physics of complex systems (i.e. foams) at scales where capillary forces predominate and the model experiments involve few well-controlled parameters [14]. Microfluidics has been applied to gas absorption processes to enhance the rate of absorption and the mass transfer in gas-liquid reactions. *Yue et al.* [15] have found that a gas-liquid microchannel contactor can provide a liquid side volumetric mass transfer coefficients and interfacial areas up to two orders of magnitude higher than other contactor (bubble columns, packed columns, tube reactors). *Kawahara et al.* [16] have investigated the velocity of bubbles, the void fraction and the pressure drop of a gas-liquid two-phase flow in a circular microchannel for distilled water and nitrogen. *Kobayashi et al.* [17] have developed an efficient system for triphase reactions such as hydrogenation reactions using a microchannel which show process for use with other multiphase reactions using oxygen and carbon dioxide. *Kawaji et al.* [18] have performed adiabatic experiments to clarify the effects of gas and liquid injection methods and inlet geometry on a two-phase water/nitrogen gas flow system in microchannels. Gas-liquid micro reactors that have a two-phase flow in micro-geometries has many advantages over analogous macro-scale reactors. An ultra-high surface to volume ratio can be achieved using a micro reactor because the micron scale linear size enhances the heat and mass transfer processes [19].

In this experiment, all reactions were conducted in a gas-liquid microreactor. Solutions with different MDEA concentrations were applied as chemical solvents and the influence of these concentrations on the absorption of H₂S was studied.

Experimental

A schematic diagram of the microfluidic device used in this study is shown in Fig. 1. The chip was fabricated in polydimethylsiloxane (PDMS) using a soft lithography technique [20]. The channels of the device were then flushed with Aquapel to make them hydrophobic, and then baking in a 65 °C oven for 20 min. The microchannel chip was measured to have channels 200 μm wide, 100 μm deep and 10 mm long. The as-prepared chip had a large specific interfacial area per volume.

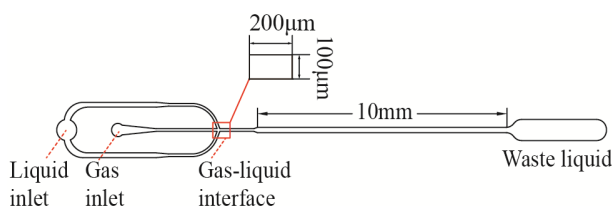


Fig. 1 – Schematic diagram of the microchannel chip.

A single push injection pump for lab (LSP01-2A) was purchased from Baoding Longer Precision Pump Co. and used in all tests. The maximum pump range was 0.166 nL - 10.831 mL/min. The microchannel chip was designed and manufactured with polydimethylsiloxane(PDMS). A high speed camera (Motionextro N4, manufactured by Integrated Design Tools Inc. USA) that could capture 3000 photos per second under maximum resolution (1024×1024) was used for imaging. A biological microscope was used as an optical source and was purchased from a Shanghai optical instrument factory.

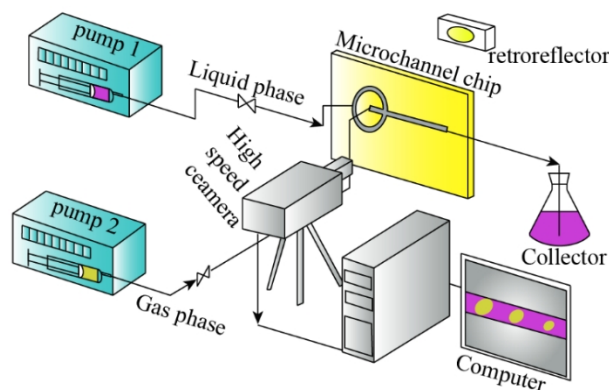


Fig. 2 – Schematic illustration of the experiment process.

This experiment was performed using a microfluidic method. A gas mixture of N_2 (70 mol%) + H_2S (30 mol%) was used as the inlet gas and a MDEA solution was prepared as the inlet liquid. A liquid medical syringe was fixed onto the liquid-phase micro-infusion pump, and gas medical syringe was fixed onto the gas-phase micro-infusion pump. The mixture gas was compressed to obtain a stable pressure and injected into the MDEA solution to form bubbles. The formation of bubbles in the interface of the gas-liquid contact was observed by high-speed camera.

Fig. 2 shows the schematic illustration of the experiment process. Solutions with different volume concentrations (20 vol%, 40 vol%, 60 vol%, 80 vol%, 100 vol%) were prepared using chemically-pure MDEA solvent and distilled water. A gas mixture of N_2 (70 mol%) + H_2S (30 mol%) was supplied by Shanghai Weichuang Standard Gas Analytical Technology Co., Ltd. with an uncertainty of 0.005. The microfluidic chip was washed using alcohol and placed onto the microscope stage. A 50 mL medical syringe was fixed onto the groove of gas-phase pump and a 10 mL medical syringe was fixed onto the groove of liquid-phase pump. The objective lens was magnified and coarse and fine adjustments were made to observe the pipeline in the microfluidic chip. The MDEA solution was then pumped into the microchannel to form a steady and continuous liquid flow. A gas mixture was then pumped into a microchannel to reach and maintain a particular gas pressure. Bubbles were then formed at the

gas-liquid interface. The precise control of flow rates (240~300 $\mu\text{L/h}$ for liquid, 1960~2450 $\mu\text{L/h}$ for gas) guaranteed bubble formation in the small channels. Each reaction was conducted under continuous-flow conditions. The gas-liquid reaction occurred quickly in the microfluidic chip so the behavior of the gas-liquid flow was monitored by a high-speed camera. The camera was either connected to a computer to record a large view photo or to a microscope to capture local details. The waste liquid from the reaction was pumped into the collector.

Results and Discussion

Fig. 3 shows the formation of bubbles at the gas-liquid interface. The camera continuously shoots 1590 photos at approximately once every 0.005 s. Fifteen pictures were selected to compare across the five MDEA solution concentrations. The size of H_2S bubble sheared by the MDEA solution was inconsistent because of the viscosity differences across the aqueous solutions. The volume of each gas bubble decreased as the gas flowed through the liquid in the small microchannel. The volume of the gas bubbles lessened over 2 s, which indicated that the methyl diethanolamine solution reacted with the H_2S in the mixture.

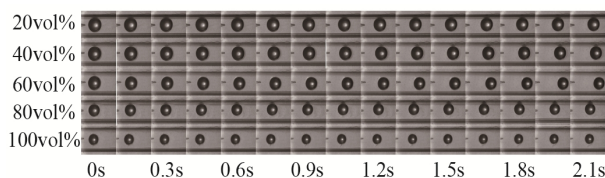


Fig. 3 – Bubble flow behavior at different concentrations.

An Image-Pro is used to measure diameters of the gas bubbles selected from Fig. 3. The volumes were calculated and drawn by Origin 8.5. For all concentrations, the volume of gas bubbles decreased linearly within 4 s. This reflects that the MDEA solution reacted with H_2S to make bubbles with a smaller volume. After 4 s, the volume of the gas bubbles stays constant. The bubbles at this point have a low concentration of H_2S gas and a certain amount of nitrogen. The MDEA solution does not react with nitrogen gas.

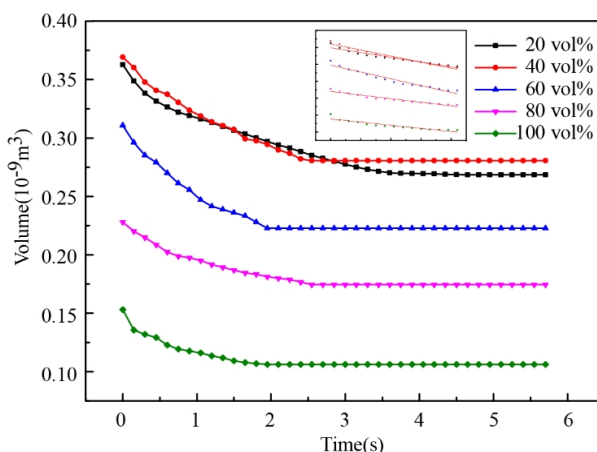


Fig. 4 – The changes in bubble volume.

Fig. 5 shows the rate of change in the volume of the gas bubbles. With a 20% volume fraction of fluid, the rate of volume change is slowest with the change lasting 4 seconds. When the volume fraction of fluid was 30%, the bubbles change size over 3 s. When the volume fractions were 60% and 80%, the bubble volume changed around 3.8% to 4.5% over 0.6 s. With a volume fraction of fluid of 100%, the bubble volume only changes over 1.8 s. The volume of the bubbles remain relatively unchanged after 4 s in all cases, at which point, the reaction between the MDEA solution and H_2S ends.

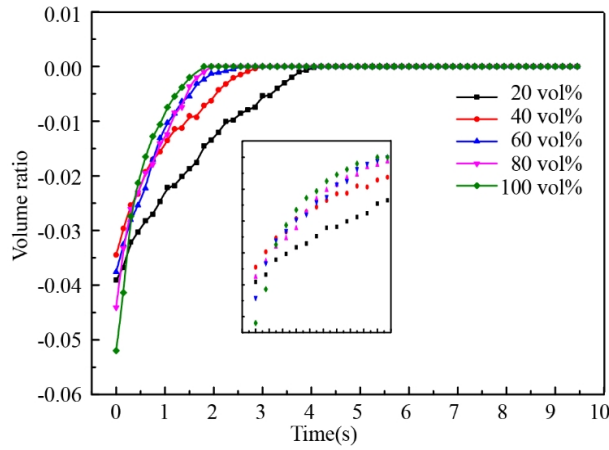


Fig. 5 – The ratio of bubbles volume change.

The liquid phase used was a water–methyl diethanolamine mixture with varying concentrations. The fluid properties of each solution are shown in Table 1.

Table 1. Fluid properties of MDEA solutions, diffusion coefficients and solubility of H₂S in corresponding liquids at 25 °C.

	MDEA content (vol%)				
	20	40	60	80	100
ρ (g ml ⁻³)	1.0169	1.0371	1.0518	1.0556	1.2313
μ (mPa s)	2.262	6.452	20.109	54.254	104.689
D (10 ⁻⁹ m ² s ⁻¹)	10235.49	4787.26	2099.7	1022.47	634.87
H (atm m ³ kmol ⁻¹)	10.35	11.54	13.79	19.15	31.44

Note: the densities and viscosity data are from Al-Ghawas et al. [21]; the diffusion and solubility data are from Rinker [22,23] and Posey [24].

It is known that when H₂S is introduced into an aqueous MDEA tertiary amine solution, it dissociates into the bisulphide ion, HS⁻, by a proton-transfer reaction:



Eq. 1 has very fast kinetics and can be considered an instantaneous reaction. It is generally accepted that a gas–liquid mass transfer rate can be described by:

$$R = k_G a (p^0 - p^*) = k_L a E (C^* - C^0) \quad (2)$$

where p^0 is the partial pressure of H₂S in the gas bulk, p^* is the partial pressure of H₂S in equilibrium with the liquid phase, C^* is physical solubility of H₂S in MDEA, C^0 is H₂S concentration in MDEA, $k_G a$ and $k_L a$ are the overall mass transfer coefficients for H₂S, and E is the enhancement factor.

In term of Henry's law, a gas–liquid equilibrium can be achieved at the interphase with a relationship described by:

$$p = HC^* \quad (3)$$

The concentration of H₂S in the liquid phase can be neglected, i.e. $C_{\text{H}_2\text{S}}^0 \approx 0$ [25,26]. The mass transfer of the gas bubbles can then be correlated with the bubble shrinkage rate by the Lagrange method [27,28]. The mass balance of the gas phase in a single bubble can be obtained as:

$$\frac{dV_B}{dt} = -k_L a (C^* - C^0) V_L \frac{RT}{P} \quad (4)$$

where V_L and V_B denote the volume of the liquid and the gas bubble, respectively.

By fitting the bubble volume at different times, the liquid side volumetric mass transfer coefficient $k_L a$ can be determined (Fig. 6). Coefficient $k_L a$ is found to increase with increasing MDEA concentration.

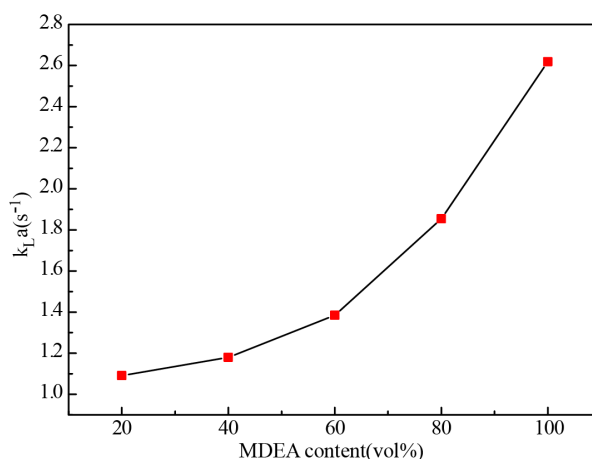


Fig. 6 – The liquid side volumetric mass transfer coefficient k_La in various aqueous solutions of MDEA.

Conclusion

A process analysis of H_2S absorption in a microchannel was investigated. Visualization experiments using a high speed camera were performed to study the evolution of gas bubble of varying sizes along the channel. The size of the H_2S bubbles formed in the MDEA fluid varies by MDEA concentration and by the distance into the liquid-filled channel. The volume of the gas bubbles lessens over 2 s, which indicates that the methyl diethanolamine in the solution reacts with H_2S . This results in a decrease in the gas content in the bubbles and, therefore, a decrease in the size of the bubbles. The rate of change of the volume was different for 20 vol% and 40 vol% concentration. However, a more rapid change of 3.8% - 5.3% volume occurs within 0.6 s when the concentration was 60 vol%, 80 vol%, and 100 vol%. The overall mass transfer coefficient for H_2S was calculated and the liquid side volumetric mass transfer coefficient k_La was found to increase as the MDEA content in the liquid phase was increased.

Acknowledgements

This work was supported by the sponsorship of the National Natural Science Foundation of China (Grant No.51308215).

References

- [1] A. Haghtalab, A. Afsharpour, Solubility of CO_2+H_2S gas mixture into different aqueous N-methyldiethanolamine solutions blended with 1-butyl-3-methylimidazolium acetate ionic liquid, *Fluid. Phase. Equilibr.* 406(2015) 10–20.
- [2] R. C. Sahu, R. Patel, B. C. Ray, Removal of hydrogen sulfide using red mud at ambient conditions, *Fuel. Process. Technol.* 92(2011) 1587–1592.
- [3] J. Song, X. Niu, L. Ling, B. Wang, A density functional theory study on the interaction mechanism between H_2S and the α - $Fe_2O_3(0001)$ surface, *Fuel. Process. Technol.* 115(2013) 26–33.
- [4] J. G. Lu, Y. F. Zheng, D. L. He, Selective absorption of H_2S from gas mixtures into aqueous solutions of blended amines of methyldiethanolamine and 2-tertiarybutylamino-2-ethoxyethanol in a packed column, *Sep. Purif. Technol.* 52(2006) 209–217.
- [5] A. Haghtalab, A. Shojaeian, Modeling solubility of acid gases in alkanolamines using the nonelectrolyte Wilson-nonrandom factor model, *Fluid. Phase. Equilibr.* 289(2010) 6–14.

- [6] B. P. Mandal, S. S. Bandyopadhyay, Simultaneous absorption of carbon dioxide and hydrogen sulfide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine, *Chem. Eng. Sci.* 60(2005) 6438–6451.
- [7] M. Bolhàr-Nordenkamp, A. Friedl, U. Koss, T. Tork, Modelling selective H₂S absorption and desorption in an aqueous MDEA-solution using a rate-based non-equilibrium approach, *Chem. Eng. Process.* 43(2004) 701–715.
- [8] S. Komati, A. K. Suresh, CO₂ absorption into amine solutions a novel strategy for intensification based on the addition of ferrofluids, *J. Chem. Technol. Biot.* 83(2008) 1094–1100.
- [9] B. Yoosuka, T. Wongsangab, P. Prasassarakich, CO₂ and H₂S binary sorption on polyamine modified fumed silica, *Fuel.* 168(2016) 47–53.
- [10] M. Taheria, A. Mohebbia, H. Hashemipoura, A. M. Rashidib, Simultaneous absorption of carbon dioxide (CO₂) and hydrogen sulfide (H₂S) from CO₂–H₂S–CH₄ gas mixture using amine-based nanofluids in a wetted wall column, *J. Nat. Gas. Sci. Eng.* 28(2016) 410–417.
- [11] T. N. G. Borhani, M. Afkhamipour, A. Azarpour, V. Akbari, S. H. Emadi, Z. A. Manan, Modeling study on CO₂ and H₂S simultaneous removal using MDEA solution, *J. Ind. Eng. Chem.* 34(2016) 344–355.
- [12] H. R. Godini, D. Mowla, Selectivity study of H₂S and CO₂ absorption from gaseous mixtures by MEA in packed beds, *Chem. Eng. Res. Des.* 86(2008) 401–409.
- [13] G. M. Whitesides, The origins and the future of microfluidics, *Nature.* 442 (2006) 368–373.
- [14] A. Huerre, V. Miralles, M. C. Jullien, Bubbles and foams in microfluidics, *Soft Matter*, 10(2014) 6888–6902.
- [15] J. Yue, G. W. Chen, Q. Yuan, L. G. Luo, Y. Gonthier, Hydrodynamics and mass transfer characteristics in gas–liquid flowthrough a rectangular microchannel, *Chem. Eng. Sci.* 62(2007) 2096–2108.
- [16] A. Kawahara, M. Sadatomi, K. Nei, H. Matsuo, Experimental study on bubble velocity, void fraction and pressure drop for gas–liquid two-phase flow in a circular microchannel, *Int. J. Heat. Fluid. Fl.* 30(2009) 831–841.
- [17] J. Kobayashi, Y. Mori, K. Okamoto, R. Akiyama, M. Ueno, T. Kitamori, S. Kobayashi, A Microfluidic Device for Conducting Gas-Liquid-Solid Hydrogenation Reactions, *Science.* 304(2004) 1305–1308.
- [18] M. Kawaji, A. Kawahara, K. Mori, M. Sadatomi, K. Kumagae, Gas–liquid twophase flow in microchannels: the effects of gas–liquid injection methods, In: *Proceedings of the 18th National and Seventh ISHMT–ASME Heat Transfer Conference*, (2006) 80–89.
- [19] J. Yue, L.G. Luo, Y. Gonthier, G. W. Chen, Q. Yuana, An experimental investigation of gas–liquid two-phase flow in single microchannel contactors, *Chem. Eng. Sci.* 63(2008) 4189–4202.
- [20] A. R. Abate, D. A. Weitz, Air-bubble-triggered drop formation in microfluidics, *Lab Chip*, 11(2011) 1713–1716.
- [21] H. A. Al-Ghawas, D. P. Hagelesche, G. Rulz-Ibanez, O. C. Sandall, Physicochemical Properties Important for Carbon Dioxide Absorption in Aqueous Methyldiethanolamine, *J. Chem. Eng. Data.* 34(1989) 385–391.
- [22] E. B. Rinker, O. T. Hanna, O. C. Sandall, Asymptotic Models for H₂S Absorption into Single and Blended Aqueous Amines, *AIChE. J.* 43(1997) 58–63.

- [23] E. B. Rinker, O. T. Hanna, O. C. Sandall, Physical Solubility of Hydrogen Sulfide in Several Aqueous Solvents, *Can. J. Chem. Eng.* 78(2000) 232–236.
- [24] M. L. Posey, G. T. Rochelle, A Thermodynamic Model of Methyldiethanolamine - CO₂ - H₂S – Water, *Ind. Eng. Chem. Res.* 36(1997) 3944-3953.
- [25] Y.G. Li, A.E. Mather, Correlation and prediction of the solubility of CO₂ and H₂S in aqueous solutions of methyldiethanolamine, *Ind. Eng. Chem. Res.* 36(1997) 2760–2765.
- [26] A. Vrachnos, G. Kontogeorgis, E. Voutsas, Thermodynamic modeling of acidic gas solubility of MEA, MDEA and MEA–MDEA blends, *Ind. Eng. Chem. Res.* 45(2006) 5148–5154.
- [27] C. Q. Yao, Z. Y. Dong, Y. C. Zhao, G. W. Chen, An online method to measure mass transfer of slug flow in a microchannel, *Chem. Eng. Sci.* 112(2014) 15–24.
- [28] C.O. Vandu, H. Liu, R. Krishna, Mass transfer from Taylor bubbles rising in single capillaries, *Chem. Eng. Sci.* 60(2005) 6430–6437.