

Absorption of Carbon Dioxide into

I) Aqueous Solutions of *N,N*-dimethylethanolamine

II) Aqueous Blends of Mono and Diethanolamine with *N,N*-dimethylethanolamine

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Absorption rates of CO₂ into aqueous solutions of *N,N*-dimethylethanolamine (DMEA) and blends of monoethanolamine (MEA) and diethanolamine (DEA) with DMEA were measured in a stirred cell and atmospheric pressures. The influence of gas flow rate, temperature and liquid concentration on the absorption rates of CO₂ into aqueous solutions of DMEA, was studied. The results show that the absorption rate of CO₂ increases with increasing gas flow rate (3–7 L min⁻¹), liquid temperature (16–32 °C), and solvent concentration (1.11–3.24 mol L⁻¹). In the next step, small amounts of MEA and DEA were added to DMEA solutions, and the absorption of CO₂ into these blends was studied. The results show that the addition of small amounts of MEA and DEA to DMEA solutions results in a significant enhancement of CO₂ absorption rates.

Key words:

Gas absorption, carbon dioxide, *N,N*-dimethylethanolamine, mixed amines

Introduction

The absorption of acidic gases, such as CO₂ and H₂S in alkali solutions, is a usual and important industrial process especially in the sweetening of natural gas and has been used for long years. Alkanolamine solutions, such as monoethanolamine (MEA) and methyldiethanolamine (MDEA), are the examples of the commonly used alkali solutions.¹

The reaction between CO₂ and amine, however, proceed at finite rates. Tertiary amines differ from primary and secondary amines in their behavior towards CO₂, since CO₂ cannot react directly with the amine group in tertiary amines. This results in smaller reaction rate between CO₂ and tertiary amines compared with primary and secondary ones.²

The reaction between CO₂ and tertiary amines has been investigated by *Haimour et al.*,² *Kim and Savage*,³ *Little et al.*,⁴ *Cordi and Bullin.*,⁵ *Rinker et al.*⁶ and *Guo-Wen Xu et al.*⁷

In the presence of CO₂, sterically unhindered primary and secondary alkanolamines are characterized by their ability to form stable carbamate ions. Since tertiary alkanolamines lack an N-H bond, the presence of CO₂ in aqueous solutions of these amines produces only bicarbonate and carbonate ions. Addition of a sterically unhindered primary or secondary alkanolamine to a purely physical solvent, such as water, increases the CO₂ absorption capacity and rate manyfold. But, because

of the high heat of reaction associated with carbamate formation, high regeneration energy costs are incurred. A tertiary alkanolamine has a lower CO₂ absorption rate, but since the heat of reaction associated with bicarbonate and carbonate formation is much smaller, regeneration energy costs are lower.⁸

Totally, the absorption of acid gases in mixed amines has advantages over the use of single amines. The addition of a small amount of primary amine to conventional tertiary amines can enhance the rate of absorption of CO₂ to a large extent without appreciably affecting the stripping characteristics. By varying the relative concentrations of the amines, an optimum absorption system can, in principle, be designed for a specific application.⁹

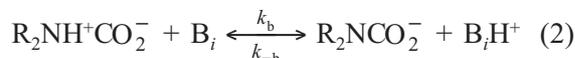
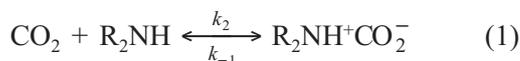
In this paper, the effects of various factors on the absorption rate of CO₂ into the aqueous solutions of DMEA as a tertiary amine, at the temperature range of 16–32 °C and atmospheric pressure, were investigated. In the next step, small amounts of MEA (as a primary amine) and DEA (as a secondary amine) were added to DMEA, and the absorption of CO₂ into this blends and the variation of the initial absorption rate, were investigated.

Theoretical

In 1968, Caplow presented a hypothesized mechanism for the carbamate (R₂NCOO⁻) formation involving the formation of an intermediate

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zwitterion. Consider the two-step zwitterion mechanism:



where B_i designates any species in solution that can act as a base to abstract the proton from the zwitterion in the second reaction step. Practically, this includes DEA, hydroxide, water, and tertiary alkanolamines.

The primary amine MEA has been studied extensively in the literature (Astarita, Barth et al., Blauwhoff et al., Danckwerts, Donaldson and Nguyen, Hikita et al., Laddha and Danckwerts, Sada et al.).^{10–17} The data for CO_2 with MEA are in very good agreement together, and all authors have found a first order dependence for the reaction rate of CO_2 with MEA, leading to the rate equation:

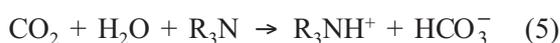
$$r_{\text{CO}_2} = k_2[\text{CO}_2][\text{MEA}] \quad (3)$$

In 1984, Blauwhoff et al. studied all of data available in the literature and concluded that the rate expression of Hikita et al. fits the data extremely well over the temperature range of 5–80 °C:

$$\log_{10} k_2 = 10.99 - \frac{2152}{T} \quad (4)$$

However, there is disagreement as to the order of reaction with respect to DEA.¹⁸

The reaction rate between CO_2 and primary, secondary, and tertiary amines is different, and it is slow in tertiary amines. The overall reaction for tertiary amines can be written as:



The following reactions can occur in aqueous solutions of tertiary amines:

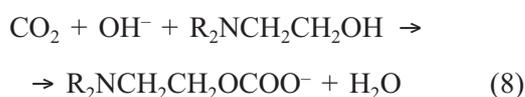
Bicarbonate formation:



Carbonic acid formation:



Alkyl carbonate formation:



Each of reactions of (6) to (8) is participated in total rate.¹⁹

Experimental

A stirred-tank absorber, shown schematically in Fig. 1, was used for absorption measurements. The absorber consisted of a 10 cm diameter cell, and the height was 17 cm. The total cell volume was approximately 1335 cm³, and 864 cm³ of liquid was used in each experiment exactly. The stirrer speed was constant in all experiments at 240 ± 5 min⁻¹. Two baffles were placed inside the cell to reduce vortex formation. The cell was kept under isothermal conditions by a water bath.

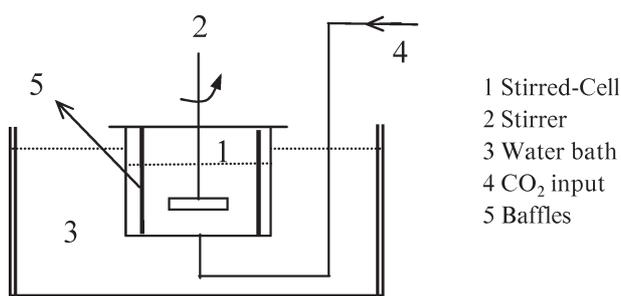


Fig. 1 – Schema of experimental apparatus

The experiments were done in the temperature range of 16 – 32 °C (± 1 °C) and atmospheric pressure. The concentration of DMEA ranged from 1.11 to 3.24 mol L⁻¹. The gas flow rate was changed from 3 to 7 L min⁻¹ (±0.2 L min⁻¹) to study the effect of gas flow rate on the rates of absorption.

For the determination of CO_2 content of the liquid, a known volume of the used alkanolamine solution was acidified with concentrated H_2SO_4 , and the volume of evolved gas measured with a gas burette^{20,21} (The error for measurement of dissolved CO_2 and, therefore, error for calculation of CO_2 absorption rate was approximately calculated equal to 7 %).

The calculation of CO_2 absorption rate by alkanolamine solutions

Plots based on concentration vs. time resulted from the experiments which have been done in this work; the equation of $c_t = c_{\text{eq}}(1 - e^{-At})$ have been found to be in agreement with the experimental results, in which c_t is the CO_2 concentration in the solution at each time, c_{eq} is the equilibrium concentration of CO_2 in the solution (constant at each experiment), and A is the coefficient which depends on temperature, gas flow rate and pressure. Experimental results were fitted to this equation using MathCAD program and A and c_{eq} calculated by the program. Differential of the equation is $\frac{dc_t}{dt} = c_{\text{eq}} A e^{-At}$ which can be

used to calculate the absorption rates in experiments. In this work, the method of initial rates²² was used to calculate the absorption rates. Calculated absorption rates are multiplied in solution volume in the cell and then divided into the contact area between gas and liquid (surface area of gas bubbles) to calculate the gas absorption rate per unit of contact area $J / \text{mol s}^{-1} \text{cm}^{-2}$.

The calculation of contact area between gas and liquid (surface area of gas bubbles)

For this purpose, the gas bubbles diameter is necessary to be determined. It can be calculated as follows:

At very slow gas flow rates²³ i.e. $Q < [20(\sigma d_0)^5 / (g \Delta \rho)^2 \rho_L^3]^{1/6}$:

$$d_b = \left(\frac{6d_0\sigma}{g \Delta \rho} \right)^{1/3}$$

Q is the volumetric gas flow rate (L min^{-1}), σ is the surface tension which is for water $72.75 \times 10^{-3} \text{ N m}^{-1}$ at $20 - 30^\circ \text{C}$,²⁴ d_0 is the orifice diameter which is in this work 0.15 cm , g is the acceleration of gravity, $\Delta \rho$ is difference in density between gas and liquid, ρ_L is the liquid density (g cm^{-3}) measured by DA-210 KYOTO ELECTRONICS densitometer ($\pm 1 \times 10^{-5} \text{ g cm}^{-3}$), and d_b is the gas bubble diameter (cm). Gas density was calculated by $\rho_G = \frac{pM}{RT}$ and was $1.53 \times 10^{-3} \text{ g cm}^{-3}$ in this work

(p is the air pressure, M is the molar mass, R is the gas constant and T is absolute temperature).

At intermediate gas flow rates²³ i.e. $Q < [20(\sigma d_0)^5 / (g \Delta \rho)^2 \rho_L^3]^{1/6}$ and $Re_o < 2100$:

$$d_b = \left(\frac{72 \rho_L}{\pi^2 g \Delta \rho} \right)^{1/5} Q^{0.4}$$

Re_o is the orifice Reynolds number and is $Re_o = d_0 v_o \rho_G / \mu_G$ in which v_o is the superficial velocity through an orifice that calculated by $v_o = \frac{Q}{A} = \frac{Q}{\pi d_0^2 / 4} = \frac{4Q}{\pi d_0^2}$, ρ_G is the gas density and μ_G is the gas viscosity. The values of μ_G for CO_2 in various temperatures are shown in the table 1.²⁴

Table 1 – The values of the gas viscosity for CO_2 in various temperatures

T / K	200	300	400	500	600
$\mu_G / \mu\text{Pa s}^*$	10.0	15.0	19.7	24.0	27.0

* $1 \mu\text{Pa s}$ (micro Pascal second) = 10^{-5} Poise

At large gas flow rates²³ i.e. $Q > [20(\sigma d_0)^5 / (g \Delta \rho)^2 \rho_L^3]^{1/6}$ and $Re_o = 10\,000$ to $50\,000$:

$$d_b = 0.0071 Re_o^{-0.05}$$

For Re_o between $2\,100$ and $10\,000$ there is no correlation. It is suggested that d_b for air – water system to be approximated by the straight line fitted to the points calculated for d_b at $Re_o = 2\,100$ and at $Re_o = 10\,000$ on log – log coordinate.²³ Our data were in this range of Q and Re_o .

The total surface area of gas bubbles can be calculated by:

$$S = S_b \cdot N_b = (4\pi)(d_b/2)^2 \cdot N_b$$

S_b is the area of one bubble and N_b is the number of bubbles that calculated from following equation:

$$N_b = \frac{V_G}{V_b} = \frac{\psi_G V_L}{(4/3\pi)(d_b/2)^3}$$

V_G is the gas volume in the gas-liquid mixture, V_L is the liquid volume in this mixture and ψ_G is the volume ratio of the gas-liquid mixture in the cell²³ and can be calculated by:

$$\psi_G = \frac{V_G}{V_L} = \frac{h_G S}{h_L S} = \frac{[(h_{L+G}) - h_L]}{h_L}$$

h_G is the height of gas, h_L is the height of liquid without gas, S is the cross section area of the absorption cell, and h_{L+G} is the height of liquid with gas. The contact area between the gas and the liquid (surface area of gas bubbles) is calculated in various gas flow rates and they are shown in the table 2.

Table 2 – The values of the contact area between the gas and the liquid in various gas flow rates

$Q / \text{L min}^{-1}$	2	3	4	5	6	7
S / cm^2	99.5	203	288	408	636	914

Results and discussion

I. CO_2 – aqueous DMEA system

Effect of gas flow rate – Fig. 2 shows the effect of gas flow rate on the absorption rates of CO_2 into aqueous solutions of DMEA. It can be seen that the absorption rate of CO_2 (in mol/s) increases with increasing gas flow rate within the range of $3-7 \text{ L min}^{-1}$, because according to table 2, the contact area between gas and solution and, therefore, the gas molecules in contact with the solution are

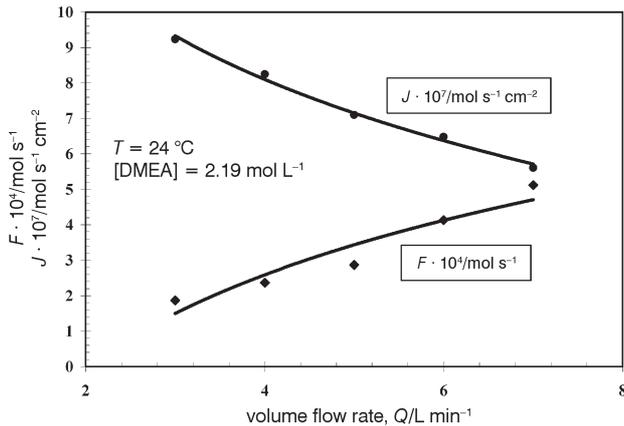


Fig. 2 – Effect of gas flow rate on absorption rate of CO_2 into aqueous solutions of DMEA, $T = 24\text{ }^\circ\text{C}$ and $[\text{DMEA}] = 2.19\text{ mol L}^{-1}$

increased with increasing gas flow rate. On the other hand, when the absorption rate calculated per unit of contact area, it ($\text{mol s}^{-1}\text{ cm}^{-2}$) decreases because contact area increases more than gas flow rate.

Effect of temperature – The rates of CO_2 absorption are plotted against temperature in Fig. 3. It is observed from figure 3 that with the rise in temperature from 16 to $32\text{ }^\circ\text{C}$ the rate of CO_2 absorption increases. The rise in temperature could decrease the viscosity of the solution and at the same time increases the molecular motions and reaction rate and, therefore, dominates over the decreasing of CO_2 solubility with temperature and, totally, the absorption rate increases. Similar findings have been reported by Yih and Sun²⁵ and Saha et al²⁰ for absorption of CO_2 in DIPA (di-isopropanolamine) and AMP (2-amino-2-methyl-1-propanol), respectively.

Effect of amine concentration – The effect of concentration of DMEA on the rates of absorption of CO_2 is shown in Fig. 4. Within the amine concentration range of $1.11 - 3.24\text{ mol L}^{-1}$, the rate of

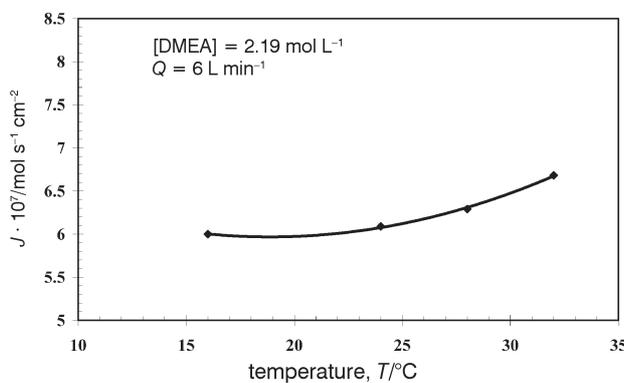


Fig. 3 – Effect of temperature on absorption rate of CO_2 into aqueous solutions of DMEA, $[\text{DMEA}] = 2.19\text{ mol L}^{-1}$ and $Q = 6\text{ L min}^{-1}$

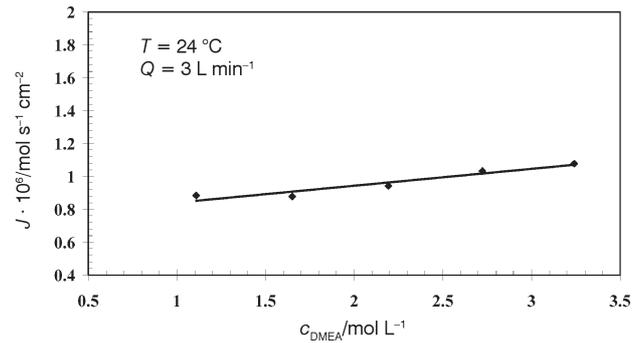


Fig. 4 – Effect of solvent concentration on absorption rate of CO_2 , $T = 24\text{ }^\circ\text{C}$ and $Q = 3\text{ L min}^{-1}$

absorption of CO_2 is seen to increase with the amine concentration.

II. CO_2 – aqueous MEA/DMEA and DEA/DMEA systems.

CO_2 absorption studies in the blended amine solutions were conducted at $24\text{ }^\circ\text{C}$. Experimental data showing concentration of CO_2 absorbed versus time for the MEA + DMEA and DEA + DMEA systems are shown in Fig. 5 and 6, respectively.

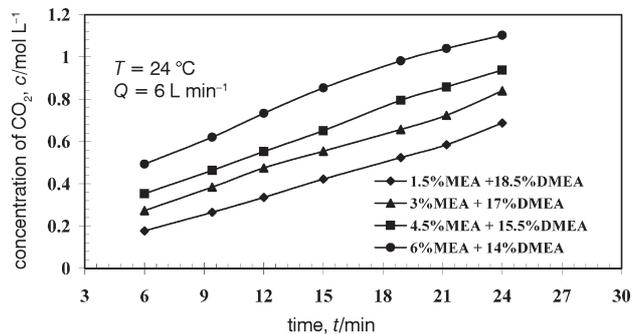


Fig. 5 – CO_2 absorption into aqueous solutions of $w = 20\%$ total amine mass fraction (MEA + DMEA), $T = 24\text{ }^\circ\text{C}$ and $Q = 6\text{ L min}^{-1}$

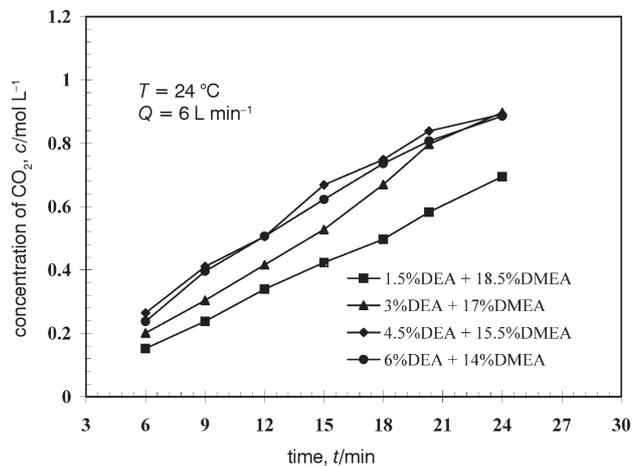


Fig. 6 – CO_2 absorption into aqueous solutions of $w = 20\%$ total amine mass fraction (DEA + DMEA), $T = 24\text{ }^\circ\text{C}$ and $Q = 6\text{ L min}^{-1}$

The results show that the addition of small amounts of MEA and DEA to DMEA results in a significant increase of absorption capacity of CO₂. This is because, primary alkanolamines such as MEA react with CO₂ in alkaline solutions, to produce stable carbamate as reaction 9 (It is also possible the protonation of MEA similar to reaction 10, but because of its low equilibrium constants in comparison with reaction 9 for MEA (Table 3), we can disregard it, in total reaction). But, tertiary alkanolamines, contrary to the primary and secondary ones (secondary alkanolamines produce unstable carbamates), are unable to produce carbamates and so, react only with CO₂ via acid – base reaction mechanism (reaction 10). The equilibrium constants which have been calculated by Daneshvar et al.²⁶ using data reported by Austgen et al.²⁷, are shown in table 3, for reactions 9 and 10 with MEA as a primary alkanolamine. MEA is more alkaline than the tertiary alkanolamines,²⁸ and so equilibrium constants of reaction of tertiary alkanolamines with CO₂ (as reaction 10) will be lower than those for MEA in reaction 10 and, therefore, in reaction 9 (discussion about DEA is similar, too). Therefore, increasing MEA / DMME or DEA / DMME ratio in absorbing solution, increasing CO₂ loading.²⁶

Table 3 – Equilibrium constants of MEA in reactions 9 and 10 at various temperatures

	303 K	318 K	333 K
Raaction 9	1.61×10^{13}	3.71×10^{12}	9.46×10^{11}
Raaction 10	5272.89	1833.48	654.69

The equilibrium constants are calculated using molar fractions and so, are dimensionless.



Fig. 7 shows the CO₂ absorption rates at different concentrations of MEA and DEA in DMEA solutions containing $w = 20\%$ of total amine mass fraction. The significant increase in absorption rate due to the addition of small amounts of MEA and DEA is evident from this figure. This is because of higher reaction rate of primary and secondary alkanolamines with CO₂ in comparison with tertiary ones.

Conclusion

The absorption of CO₂ into aqueous solutions of *N,N*-dimethylethanolamine (DMEA) in a stirred-tank absorber at atmospheric pressure and in

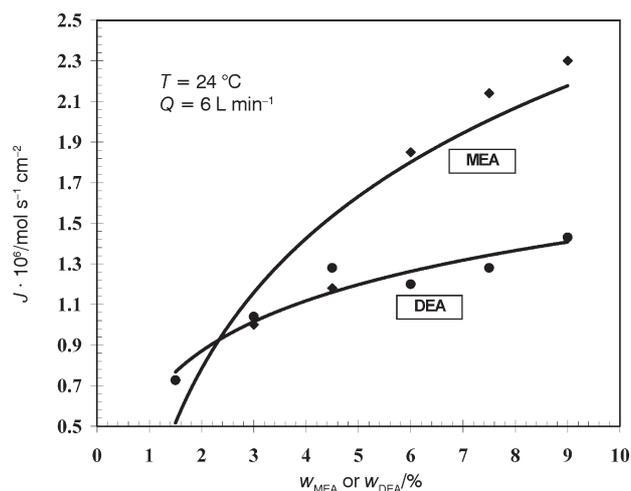


Fig. 7 – Effect of MEA and DEA mass fractions on absorption rate of CO₂ into DMEA solutions ($w = 20\%$ total amine mass fraction), $T = 24\text{ °C}$ and $Q = 6\text{ L min}^{-1}$

the temperature ranges of $16 - 32\text{ °C}$; gas flow rate of $3 - 7\text{ L min}^{-1}$; stirring rate of $n = 240\text{ min}^{-1}$; and DMEA concentration of $1.11 - 3.24\text{ mol L}^{-1}$, show that CO₂ absorption rate increases with increasing gas flow rate, liquid temperature, and DMEA concentration.

On the other hand, the addition of small amounts of MEA and DEA to aqueous solutions of DMEA results in a significant enhancement of CO₂ absorption rates. This also increases the equilibrium absorption capacity of the solution. Therefore, we can formulate the proper mixed amine solvents with lower energy consumption in regeneration step, while the absorption rate and the equilibrium absorption capacity of the solution is being in acceptable extent.

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Nomenclature

- A – area of orifice (cm²)
- c_t – concentration of CO₂, mol L⁻¹
- c_{eq} – equilibrium concentration of CO₂, mol L⁻¹
- DMEA – *N,N*-dimethylethanolamine
- DEA – diethanolamine
- d_o – orifice diameter, cm
- d_b – gas bubble diameter, cm
- Q – volumetric gas flow rate, L min⁻¹
- g – acceleration of gravity, m s⁻²
- h_{L+G} – height of liquid with gas, cm
- h_L – height of liquid without gas, cm

h_G – height of gas, cm
 M – molar mass, kg
 MEA – monoethanolamine
 N_b – number of bubbles
 p – air pressure, N m^{-2}
 J – absorption amount flux, $\text{mol s}^{-1} \text{cm}^{-2}$
 F – absorption amount flow rate, mol s^{-1}
 R – gas constant, $\text{N m kmol}^{-1} \text{K}^{-1}$
 w – mass fraction, %
 Re_o – orifice Reynolds number
 s – surface area or cross section area of the absorption cell, cm^2
 T – temperature, $^{\circ}\text{C}$
 V_b – bubble volume, L
 V_G – gas volume, L
 V_L – liquid volume, L
 v_o – superficial velocity through an orifice, m s^{-1}
 σ – surface tension, N m^{-1}
 $\Delta\rho$ – difference in density between gas and liquid, g cm^{-3}
 ρ_L – liquid density, g cm^{-3}
 ρ_G – gas density, g cm^{-3}
 μ_G – gas viscosity, $\mu\text{Pa s}$
 ψ_G – volume ratio

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