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Chapter 5

Discussions of Effects of Surface Tension on Water Vapor Absorbed by Triethylene Glycol Solution Films

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Additional information is available at the end of the chapter

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Abstract

The surface tension gradient can result from releasing a surfactant from the liquid film or feeding a vapor into the liquid film, and the interfacial disturbance will be induced by them. The flowing phenomena were termed “Marangoni effect,” and the mass transfer performance was enhanced by the effect. The objective of this study was to apply the Marangoni effect, such as water vapors absorbed by the liquid film of triethylene glycol (TEG) solution, and to analyze mass transfer behaviors with and without surfactants’ addition in the liquid film. The interfacial disturbance resulted from the surface tension gradient was considered in this study, and the mass transfer behaviors for packed-bed absorbers were discussed to elucidate the influence of the Marangoni effect on the absorbers. It was observed that the trends of mass transfer rates could be increased significantly as the surfactant is added into the absorption system. Experimental results showed that feeding a vapor or adding a surfactant with lower surface tension and/or higher volatility in the liquid will result in the surface tension gradient on the gas-liquid interface. The induced flowing disturbance will lead to an increment of mass transfer rate for a gas-liquid contact system.

Keywords: solution film, TEG solution, absorption, Marangoni, surface tension

1. Introduction

The fluid disturbance resulting from the surface tension gradient in the interface of the gas-liquid contact systems is usually called the Marangoni effect or surface tension effect. For the liquid thin film, the gas solutes are easier to dissolve into the thinner liquid film than the thicker liquid film [1], and the concentration in the thinner part would be higher than that
in the thicker part. Therefore, the surface tension gradient is formed in the interface. The Marangoni positive and negative systems can be defined by changes of the gas-liquid contacting area. The interfacial convection resulting from the Marangoni effect is usually called the Marangoni convection. The interfacial instability resulting from the surface tension is normal to the liquid surface, and it is always called the Marangoni instability. The surface tensions for absorption solutions could be measured by a surface tension meter (CBVP-A3, Kyowa Interface Co. Ltd.). The surface tension meter was based on the method for a Wilhelmy plate, as shown in Figure 1. A Wilhelmy plate is a thin plate, usually in the order of a few square centimeters in area, used to measure equilibrium surface or interfacial tension at a gas-liquid or liquid-liquid interface. The top of the plate was connected to a spring, and the spring was connected to a force sensor. The equilibrium state is reached instantaneously between the surface tension acting on the plate and the spring force pulling up the plate as the plate comes in contact with the liquid surface. According to the Wilhelmy equation, shown in Eq. (1), embedded in the surface tension meter, the surface tension for a liquid solution would be calculated and displayed on the panel.

\[ \gamma = \frac{F}{l \cos \theta} \]  

(1)

where \( \gamma \) is surface tension, \( F \) is elastic force, \( l \) is the wetted perimeter, and \( \theta \) is the contact angle between the liquid phase and the plate.

Mentioned earlier, the flow of interfacial fluid could be provoked by the Marangoni effect. The methods for inducing surface tension gradient include the design of electric field with

![Figure 1. Schematic diagram for surface tension of the liquid solution exerted the plate.](image)
ionic compounds, concentration difference, temperature difference and surfactant addition to the liquid solution. Therefore, the interfacial disturbance could be produced by solutes transferring across phases. Some studies described the relationship between the Marangoni effect and transport phenomena, which are introduced as follows.

The working electrodes were set in the experimental cell to detect the potential energy. The concentration of the ferrocenyl surfactant was decreased with the decreased potential energy and then the surfactant became the surface active matter. The experimental results showed that the velocity of Marangoni flow decreased with the decreased desorption rate of the ferrocenyl surfactant. The concentration gradient of the desorbed ion resulted from the potential energy, and the surface tension gradient was formed by the concentration gradient. Therefore, the fluid disturbance was provoked in the surface layer of the liquid solution. In addition, the concept of the solutal Marangoni effect was always used to describe the fluid flow in the liquid surface by vaporizing the volatile materials. For example, see Ref. [3]. The mixture of ethanol/water, heptane/decane, hexane/decane, and octane/decane was used to show that the liquid film climbs from a macroscopic reservoir as the volatile component with lower surface tension in the system. On the other hand, the studies about the thermal Marangoni effect focused on the convective phenomena for the bulk liquid layer with heating in the bottom. Since the heat source was from the bottom, the liquid density decreased along with the depth of the liquid solution. Therefore, the upward convection occurred due to the temperature gradient. Furthermore, the temperature of the upward fluid was still higher than the ambient liquid in the surface, and then the surface tension gradient was formed to make the outward flow radial. The local outward flow could be observed all over the liquid surface, and it was the so-called cellular-type flow. The small disturbance analysis was adopted to deduce that the surface tension gradient resulted from the change of temperature, which was large enough to produce the cellular-type flow in the liquid convective cell that was heated from the bottom.

In order to enhance the mass transfer performance for water vapor absorption by the solution in the absorption-refrigeration system, some surface additives were added to the liquid surface to activate the interfacial disturbance. N-hexanol, n-heptanol, n-octanol, 2-ethyl-hexanol, or n-nonanol was used as a surfactant to enhance the performance for water vapor absorption by the aqueous LiCl solution [5]. The experimental results showed that the interfacial disturbance occurred and the absorption capacity was enhanced in the concentration of n-octanol from 10 to 25 ppm. For the aqueous LiBr solution, adding the surfactants, except n-hexanol, induced the interfacial disturbance. The concentrations of other surfactants were controlled at 25 ppm. Besides, the absorption capacities for CO₂ absorbed by water were increased as methanol, ethanol, n-propanol, n-butanol, and n-propanol added onto the liquid surface [6]. However, the interfacial disturbance could not be observed as n-hexanol and Triton X-100 were added on the surface of water. Based on the thickness of the liquid layer, the Marangoni number was also calculated to assess the critical point for the interfacial disturbance resulting from the spreading liquid.

In addition to adding surfactants on the liquid phase, there are also some studies adding surface additives to the gas phase to discuss the effect of surface active materials on mass transfer.
performance and the relationship between mass transfer performance and interfacial disturbance. By measuring the surface tension of liquid solution, the surface tension of liquid solution affected by the vapor of 2-ethyl-1-hexanol (2EH) in the gas phase was demonstrated [7]. The experimental results showed that the effect of surface additives on surface tension was larger for adding in the gas phase than in the liquid phase. Subsequently, the dynamic theory for the absorption and desorption of 2EH on the surface of the LiBr aqueous solution was discussed [8]. The simulated results showed that the higher the vapor pressure of 2EH in the gas phase, the better the mass transfer performance for absorbing H₂O by the LiBr aqueous solution. Therefore, the mass transfer performance could be enhanced by the interfacial disturbance resulting from adding surface additives in the liquid and gas phases while the operating variables were controlled well. Discussions of the interfacial behaviors resulted from adding surfactants to the gas phase, which were limited in the literature, and the related data were rare. Mentioned earlier, the surface tension was affected by adding surfactant to the liquid and gas phases, leading to the influenced mass transfer performance by the interfacial disturbance resulting from the surface tension gradient. Therefore, the surfactant was added in the gas and liquid phases to discuss the effect of surfactant on mass transfer performance. Besides, the mass transfer performance with and without surfactant addition to the working solution in the packed-bed absorber was also compared. Not only was the relationship between mass transfer process and interfacial phenomena described but also the enhancement of mass transfer performance for the absorption system was demonstrated in this study.

2. Solution film in the mass transfer equipment

Table 1 shows some literature related to mass transfer equipment with continuous liquid phase. These mass transfer equipment include packed-bed absorber, packed-bed or tray distillation column, falling film absorber, concentric absorption system, and bubble absorber. Except for bubble absorber [9, 10], a continuous liquid phase was presented as a solution film in the mass transfer equipment for all others. As mentioned by Wu [11], the Marangoni effect could be triggered in mass transfer systems with continuous liquid phases. Therefore, mass transfer behaviors that occurred in the solution film are discussed in this article.

In order to discuss the spontaneous Marangoni effect in the absorption process, an absorber packed closely with cylindrical packing was designed [11]. The solution flow rate was controlled under the state of laminar flow. Since the surface tension of water vapor is larger than that of TEG solution, the spontaneous Marangoni effect is triggered by absorbing water vapor in the solution film. Although the mass transfer performance could be enhanced by adding a promoter in capturing CO₂ by potassium carbonate (KCO₃), the pressure drop and holdup increased in the packed absorption column. For example, see Ref. [12]. Glycine was added to K₂CO₃ solution film to examine the enhancement of the CO₂ absorption. In addition to adding surface additives, the Marangoni instability could also be produced by the temperature dependence of the surface tension, such as nonlinear model of the instability in gas absorption was developed [13] to discuss the performance for carbon dioxide absorbed by water. Recently, the structured packings with different thickness and channel angles were designed [14] to study effect of packings and surface additives on the performance of water vapor absorbed by LiCl film.
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Table 1. Some literature related to mass transfer equipment with continuous liquid phase.
Based on the concept of Marangoni effect acting on the thin liquid film, the system n-heptane/methylcyclohexane was used [15] to discuss the effect of positive and negative driving force on different packings. The criteria for determining the positive or negative driving force for the packed-bed distillation column were based on the packings; however, the criteria for determining the positive or negative Marangoni effect was decided by the mixture. The systems included methanol/water, methanol/isopropanol, and water/acetic acid, which were used to discuss the effective interfacial area for the positive, negative, and neutral Marangoni systems [16]; the systems included methanol-water, methanol-2-propanol, and n-heptane-toluene [17] to elucidate the relationship between froth stabilization and interfacial area; the systems included methanol/isopropanol and methanol/water [18] to describe the solution film affected by the Marangoni effect.

In addition to the packed-bed absorber, the falling film or wetted wall column was also applied for the absorption process widely. 2EH was used as an additive in the vertical falling film to discuss heat and mass transfer enhanced by the Marangoni convection [19, 20]. Furthermore, the flat copper plate and the copper plate covered with a copper wire screen were also tested to observe the Marangoni convection resulting from adding 2EH to the solution film [20]. In contrast with water vapor absorbed by aqueous lithium bromide solution, carbon dioxide absorbed by aqueous monoethanolamine (MEA) solution could be regarded as a chemical absorption process. Since the surface tension of the absorbent solution was changed by a chemical absorption process, the Marangoni effect was always accompanied with this process. For example, see Refs. [21, 22]. CO$_2$ absorbed by the MEA solution was conducted, and the mass transfer enhancement and the cellular convection were discussed and observed.

Whatever gradient in surface tension resulted from spontaneous or artificial absorption process, it is difficult to observe by naked eye or scientific apparatus. Since the induced Marangoni convection and Marangoni instability were microscopic phenomena, they could be recorded or observed by scientific or special apparatus. On the basis of the difficult observation, some experimental systems were designed to demonstrate the mass transfer performance enhanced by the Marangoni effect, such as the concentric absorption system. Generally speaking, the surface additive with lower surface tension was injected by a capillary tube into the center of the absorption cell. For example, see Ref. [23]. Methanol, ethanol, propanol, and acetone were used as surface additives, respectively, to discuss absorption of CO$_2$ by water and surfactant solution in the presence and absence of Marangoni effect. Not only the liquid additive in the liquid surface but also vapor additive in the absorption system were carried out to analyze enhancement of mass transfer performance by the Marangoni effect for water vapor absorbed by LiCl solution [24].

The concept of packed-bed absorber was also the solution film that flowed over packing materials so that a series of experiments were performed to discuss absorption of water vapor by TEG solution and to elucidate the relationship between interfacial disturbance and mass transfer behaviors. TEG solution was used as a working solution to absorb water vapor in the packed-bed absorber, as shown in Figure 2, and the packing materials were 5/8-inch polypropylene flexi rings. The system can handle air flow rates from 1.35 to 1.58 kg/m$^2$ s and liquid flow rates from 0.6 to 0.9 kg/m$^2$ s. The flow meters and flow controller used in this study
were calibrated by standard procedures. The absorbent solution was brought into the packed bed by the liquid pump and distributed over the packed bed by the nozzle. The liquid flow rates were controlled by rotameter. The air flow rates were adjusted by 0.5 HP blower and transistor inverters. The liquid film, flowed on the packing, contacted the gas phase in the packed-bed absorber and absorbed water vapor successfully. After a series of experimental tests (3–4 runs) were completed, the absorption system was heated to raise the temperature of the TEG solution. Once the heated solution contacted with the process air, the water molecules in the absorbent solution were stripped from the TEG solution. The regenerated TEG solution could be reused in the next series of experimental tests. Besides, a Rotronic IDL 20 K hygrometer with two humidity probes, which can measure the humidity from 0 to 100% RH

![Experimental apparatus of this study.](image)

**Figure 2.** Experimental apparatus of this study.
at −20 to 60°C, was used in this study. The concentration of the TEG solution was measured by a refractometer. The cross-section area of the packed bed and air tunnel was 15*15 cm², and the height of packing was 45 cm. The absorption capacity could be calculated by the inlet and outlet humidity to discuss effect of operating variables on mass transfer performance.

The water vapors were absorbed by 93 wt.% TEG solution and 93 wt.% TEG solution with 5 wt.% ethanol, respectively. Therefore, effect of operating variables on mass transfer performance was discussed, and absorption capacities with and without surface additives added to the TEG solution were compared. On the other hand, the ethanol vapor was injected in the gas phase to discuss mass transfer difference between the additive adding in the liquid and gas phases.

3. Discussions for mass transfer

3.1. Mass transfer results for solution film in the equipment

A series of experiments presented in this article were water vapor absorbed by the TEG solution films in the packed-bed absorber. Therefore, some results related to solution film in the mass transfer equipment were described as follows.

For packed-bed absorber, the effective interfacial area is increased for the positive Marangoni effect. Absorption of water by LiCl solution [14] found that the surface area was larger for a 30° channel angle and 6 mm thickness packing material. Therefore, the maximum heat and mass transfer performance were 0.4 for COP and 85% for dehumidification efficiency. Since the foam resulted from addition of surface additive would hinder mass transfer process, addition of surface additive into the LiCl solution did not helpful. For absorption of water vapor by TEG solution [11], results showed that the mass transfer performance was larger for concentration of TEG solution greater than 92 wt.% Since the surface tension of water vapor was higher than that of TEG solution, the surface tension of TEG solution is increased during the absorption process. The coverage of the higher concentration of TEG solution on the packing surface was wider than the lower concentration due to the difference in surface tension. The coverage of TEG solution on the packing surface resulted from increment in surface tension, which could be termed as a positive Marangoni effect for the absorption system.

For the gradient in surface tension, the Marangoni effect in the packed-bed distillation column was divided into a positive and a negative system. Transportation of a component with lower surface tension from a liquid phase to a gas phase may increase surface tension in the surface of the transferred spot. Since the surface tension for the transferred spot is higher than the surrounding liquid, the surrounding liquid is drawn to the transferred spot. The flow phenomenon driven by this process may spread over the packing well in the packed-bed distillation column and increase mass transfer performance. Therefore, the system, making a more effective area on the packing, is termed “positive system.” On the contrary, transportation of a component with high surface tension from a liquid phase to a gas phase may decrease surface tension in the surface of the transferred spot. Since the surface tension for the transferred spot is lower than the surrounding liquid, the induced stress is directed from the transferred spot to the surrounding liquid. The flow phenomenon may lead the packing surface to be contrasted.
Since the mass transfer performance would decrease with the decreased effective area, such a system is termed “negative system.” Therefore, the surface refreshment was affected by the smaller packing and the lower liquid flow rates more significantly [15]. Three systems include organic and aqueous systems, Marangoni positive (methanol/water), neutral (methanol/isopropanol), and negative (water/acetic acid) systems, which were used to develop a mass transfer model for a distillation column packed with the structured packing [16]. The results showed that the effective area was larger for the positive system than that of the negative system due to the more stable liquid film. Besides, the experimental results also demonstrated that the better liquid distribution or more stable liquid film on the packing surfaces resulted from the positive effect, methanol/water, to increase mass transfer performance [18]. In addition to the packed distillation column, the interfacial area for the positive system in a tray distillation column also increased with the stabilized froth [17].

2EH was used as an additive to enhance absorption of water vapor by the LiBr solution film in the falling film system [19, 20]. Enhancement of heat transfer could be caused significantly by small amounts of additives during absorption process, and the enhanced degree was decided from the additive concentration and Reynolds number [19]. Besides, 2EH was also used as an additive in the system of the vertical falling film, and flat copper plate and the copper plate covered with a copper wire screen were tested by LiBr solutions with and without 2EH [20]. The experimental results showed that twice the heat transfer was enhanced by adding 2EH in LiBr-water films on the bare copper surface and approximately 2.5 and 3.5 times the mass transfer was enhanced by adding 2EH in LiBr-water films on the bare copper surface in adiabatic and water-cooled absorption, respectively. The Marangoni effect resulted from chemical absorption, which was applied for absorption of CO$_2$ by aqueous MEA solution in the falling film systems [21, 22]. A model was assumed that the cellular convection was driven by the gradient in surface tension, which was induced by infinitesimally small perturbations of concentration [21]. The numerical results demonstrated that the minimum gas-liquid contact time was necessary for the convection to occur, and the time turned out to be below 0.01 s. In order to measure the mass transfer rate affected by the Marangoni effect in a microreactor and to compare this rate with the value for the analogous process without Marangoni effect, a falling film microreactor (FFMR) with 29 microchannels was designed and investigated for the gas-liquid mass transfer process [22]. The appearance of the Marangoni effect in a falling film microreactor was observed, which was accompanied with absorption enhancement when increasing amine concentrations under the condition of lower partial pressures of CO$_2$. The experimental results also showed that a 3–6-fold increase in the absorption rate is observed for MEA concentrations in the range from 2 to 2.5 M.

For the concentric absorption system, methanol, ethanol, propanol, and acetone were added, respectively, to the water surface to induce interfacial disturbance [23]. The results showed that absorption of CO$_2$ was enhanced by the interfacial disturbance. Sodium lauryl sulfate (SLS) and cetyltrimethylammonium bromide (CTMAB) were used as a surfactant, respectively, to test the performance of carbon dioxide absorbed by water. Enhancement of mass transfer performance for carbon dioxide absorbed by water was demonstrated for water surface adding 20–100 wt.% aqueous solution of methanol, ethanol, and 2-propanol. Increment of mass transfer performance with the increased surfactant concentration was also observed. In addition, the ethanol vapor and the ethanol droplets from capillary were added, respectively, to the
absorption system [24]. Since the Marangoni effect was more pronounced for the concentration of LiCl greater than 40 wt.%, the experimental results showed that the removal efficiencies were increased significantly beyond 40 wt.%. Absorption enhancement was better for ethanol vapor than for ethanol droplets, which was also demonstrated.

3.2. Influences of operating variables for the presented study

As shown in Figure 3, the removal of H$_2$O by the TEG solution was decreased with the increased liquid temperature. Since the driving force for H$_2$O absorbed by the desiccant solution is determined by the depression of water vapor pressure, the water vapor will be transferred from the bulk gas phase with the higher vapor pressure to the gas-liquid interface with the lower vapor pressure. The vapor pressure of desiccant solution was lower for the lower liquid temperature, and the depression of water vapor pressure would be larger for the lower liquid temperature. Therefore, the lower the liquid temperature, the higher the mass transfer performance. Similarly, the vapor pressure of the TEG solution was decreased with the increased concentration, and the depression of vapor pressure was larger for the higher TEG concentration. The larger depression of vapor pressure would lead to the larger driving force for H$_2$O absorbed by the TEG solution. Therefore, the removal amount of H$_2$O increased with the increased TEG concentration, as shown in Figure 4. Figure 5 showed that the removal amount of H$_2$O by the TEG solution decreased when the air flow rate increased. Since the amount of treated H$_2$O was increased with the increased air flow rate, the mass transfer performance was lowered with the increased air flow rate. On the other hand, the higher air flow rate reduced the time for water vapor exposed to the liquid surface so as to reduce the

![Figure 3](image-url)  
Figure 3. Effect of liquid temperature on removal amount.
exposure time and to decrease the absorption capacity. According to these points of view and the experimental results, the removal amount of H\textsubscript{2}O by the TEG solution decreased with the larger air flow rate. In contrast, the removal amount of H\textsubscript{2}O by the TEG solution was increased when the liquid flow rate was increased, as shown in Figure 6. Since the TEG solution was used as the working solution for absorption of water vapor in the gas phase, the higher mass transfer performance would be accompanied with the larger liquid flow rate. On the other hand, the larger liquid flow rate would promote the phenomenon of surface renewal. It could be thought that the absorption site increased in the packed-bed absorber and the mass transfer performance was increased. Therefore, Figure 6 showed that the removal amount of H\textsubscript{2}O was increased with the increased liquid flow rate. Since the explanations of the effect of operating variables on mass transfer performance for TEG solution with surfactants were similar as that for the TEG solution without surfactants, the descriptions for the mass transfer performance affected by operating variables were neglected under the condition of adding surfactants.

3.3. Influences of additives for the presented study

As shown from Figures 3–6, the removal amounts were always larger for the TEG solution with ethanol than without ethanol. The results can be explained by two points of views. Ethanol molecules would vaporize from the TEG thin film in the packed-bed absorber. The gradient in surface tension would result from the vaporization of ethanol, and the interfacial disturbance would be formed by the gradient in surface tension. The probability of water vapor contacted with the TEG solution film would increase with the formed interfacial disturbance. Therefore, the mass transfer performance would be enhanced by adding ethanol to the TEG solution. On

![Figure 4](http://dx.doi.org/10.5772/intechopen.76148)

Figure 4. Effect of TEG concentrations on removal amount.
Figure 5. Effect of air flow rate on removal amount.

Figure 6. Effect of liquid flow rate on removal amount.
the other hand, the packing area was always not wetted completely in the absorption process. Vaporization of ethanol would be easier in the interface between the TEG-solution thin films and non-wetted packing surface, that is, the rate of vaporization of ethanol for the thinner liquid film would be larger than the thicker liquid film. Furthermore, the surface tension of the TEG solution was larger than ethanol so the surface tension of the thinner liquid film would be larger than the thicker liquid film. Therefore, the gradient in surface tension would be provoked by vaporization of ethanol, and the liquid film would be spread on the packing surface more widely. Therefore, the gas-liquid contacting area was increased and the mass transfer performance would be enhanced. Since the surface tension affected by temperature was not significant, the difference of the removal amounts with and without ethanol was smaller than other variables, as shown in Figure 3.

4. Conclusions

Since the interfacial fluid flow could be provoked by the surface tension gradient, the volatile matter was used as an additive in this study to discuss the effect of additive on mass transfer performance. Therefore, not only experimental mass transfer rates for water vapor absorption into the TEG solutions under different operating conditions were reported but also mass transfer performance with and without adding additives were also compared in this study. The removal amount of H$_2$O increased with the higher TEG concentration and liquid flow rate; however, the removal amount of H$_2$O decreased with the lower liquid temperature and air flow rate. Besides, the interfacial disturbance that resulted from addition of surface additive made the absorption ability of the TEG solution with ethanol higher than that without ethanol. According to the following deductions, the mass transfer performance was enhanced by adding ethanol to the TEG solution. The first is that the vaporizing ethanol would result in the surface tension gradient to form the interfacial disturbance, and the probability of gas-liquid contact is increased. The second is that the surface tension gradient would result from the vaporization of ethanol, and the formed surface tension gradient would prompt the TEG solution thin film to spread on the packing surface more widely. Therefore, the better removal amount of H$_2$O for the TEG solution with ethanol was demonstrated by the experimental results in this study.

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