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Heat transfer enhancement by additive in vertical falling film absorption of H₂O/LiBr

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Abstract

The enhancement effects of additive on vertical falling film of water into aqueous lithium bromide (LiBr) were studied by an experimental method. Based on the Navier–Stokes equations of falling film absorption, a new dimensionless parameter, surface renewal number Rn , was introduced, and a semi-empirical equation of enhancement factor of additive was obtained. It was shown that the absorption Marangoni number Ma , the surface Marangoni number M_{aA} , and the surface renewal number Rn enhance the heat transfer of absorption, however the adsorption number Π and the Reynolds number Re weaken the heat transfer of absorption. It was proved that the semi-empirical equation agreed well with the experimental results by introduction of the parameters related to surface tension characters presented by the authors into the equation.

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Keywords: Additive; Falling film absorption; Heat transfer; Enhancement factor

1. Introduction

Heat and mass transfer in the absorber of a LiBr absorption chiller can be enhanced significantly with the addition of small amount of additives, such as 2-ethyl-1-hexanol (2EH), 1-octanol and so on. It is widely agreed that the heat and mass transfer can be enhanced obviously due to an

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Nomenclature

a	equilibrium coefficient for additive in solution side
A	area (m ²)
b	equilibrium coefficient for additive in gas side
Bi_c	Biot number
c_{cw}	specific heat capacity of cooling water (J/kg °C)
Cr	Crispation number, defined by Eq. (44)
d_i	inner diameter of absorption tube (m)
d_o	outer diameter of absorption tube (m)
D_A	diffusivity for additive in aqueous LiBr (m ² /s)
D_w	diffusivity for water in aqueous LiBr (m ² /s)
E	absorption number
g	gravitational acceleration (m/s ²)
h	heat transfer coefficient (W/m ² °C)
h_c	heat transfer coefficient of cooling water (W/m ² °C)
k	thermal conductivity of aqueous LiBr (W/m °C)
k_s	thermal conductivity of absorption tube (W/m °C)
L	effective length of absorption tube (m)
m_{cw}	mass flow rate of cooling water (kg/s)
Ma	absorption Marangoni number, defined by Eq. (46)
Ma_A	surfactant Marangoni number, defined by Eq. (47)
Nu	Nusselt number
Nu_0	base Nusselt number during the absorption without additive
p	pressure (pa)
Pr	Prandtl number of aqueous LiBr
Q	total absorber heat transfer rate (W)
Re	Reynolds number for falling film
Rn	renewable number, defined by Eq. (48)
Sc_w	Schmidt number of water in aqueous LiBr
Sc_A	Schmidt number of additive in aqueous LiBr
t	time (s)
T	temperature (°C)
$T_{cw,i}, T_{cw,o}$	temperature of cooling water at inlet and outlet of absorber, respectively (°C)
T_e	equilibrium temperature of aqueous LiBr at concentration X_{wo} (°C)
T_i, T_o	temperature of aqueous LiBr at inlet and outlet of absorber, respectively (°C)
\mathbf{u}	(u, v) with u and v the velocity components in the z - and y -directions (m/s)
U	overall heat transfer coefficient (W/m ² °C)
U_m	maxium velocity of falling film at y direction (m/s)
U_a	average velocity of falling film at y direction (m/s)
X_A	bulk concentration of additive in aqueous LiBr
X_g	relative mass concentrations of additive in gas side

X_1	relative mass concentrations of additive in solution side
X_w	bulk concentration of water in aqueous LiBr
$X_{w,e}$	equilibrium concentration of water in aqueous LiBr at temperature T_i

Greek letters

δ	thickness of film
σ	surface tension (mN/m)
σ_0	surface tension of aqueous LiBr without any additive (mN/m)
σ_c	critical surface tension (mN/m)
σ_t	dynamic surface tension (mN/m)
ν	kinematic viscosity of aqueous LiBr (m ² /s)
μ	dynamic viscosity of aqueous LiBr (N s/m ²)
Γ	additive surface-excess concentration (kg/m ²)
Γ_c	critical additive surface-excess concentration (kg/m ²)
η	surface deformation of falling film
α	thermal diffusivity of aqueous LiBr film
α_{Nu}	enhancement factor, defined by Eq. (49)
ρ	density (kg/m ³)
λ	absorption heat (W/kg)
Π	adsorption number, defined by Eq. (45)

Subscripts

i	parameters at inlet of absorber
o	parameters at outlet of absorber
s	unperturbed part of a dimensionless variable

Superscripts

*	dimensionless variable
'	infinitesimal perturbation part of a dimensionless variable

interfacial convection, named Marangoni convection, which is driven by surface tension gradients caused by non-uniform surface concentration of additive.

The Marangoni convection has been understood in qualitative terms and have guided numerous experiments investigating the enhancement effect of additive, however a solid quantitative understanding has not been developed fully because of uncertainties in some key aspects of absorption process with additive which include: (1) enhancement mechanism of additive [2,5,9,13,14,16], (2) physical properties of aqueous lithium bromide with additive; and (3) the complicated nature phenomena of Marangoni convection in the presence of additive. Ji and Setterwall [8] analyzed falling film absorption process in the presence of additive by an extensive linear stability theory, and predicted the major parameters influencing the hydrodynamic stability in such system. On the basis of the salting out effect, Daiguji et al. [2] investigated the Marangoni convection using a linear stability analysis, and estimated the vapor absorption augmentation in an adiabatic static pool by the numerical simulation of cellular convection. Koenig et al. [12]

developed a 2D numerical model to describe the absorption of a high heat-of-absorption vapor into a static horizontal liquid film containing small concentration of an additive.

This paper focused on the enhancement of heat transfer induced by additive in vertical falling film absorption of water vapor into aqueous LiBr. According to on the analysis of Navier–Stokes equations, some dimensionless parameters related to the enhancement effect were introduced. Based on the surface tension model presented by the authors [1], a semi-empirical equation of enhancement factor of heat transfer in the vertical falling film absorption was developed. The semi-empirical equation agreed well with the experimental results presented in this paper.

2. Surface tensions of aqueous LiBr with additives

The effect of an additive on the surface tension of aqueous LiBr is the key reason leading to the Marangoni convection. However, the experimental data of surface tension published in literature are not sufficient, and even some of them are scattered and inconsistent [6,7,10,11,13–15].

The authors measured the surface tension of aqueous LiBr with additive 2EH and 1-octanol by using a Wilhelmy plate method, respectively. The experimental results showed that the surface tensions of 55% LiBr solution with additive are oscillatory while the solution is exposed to air. The oscillations were shown in Fig. 1.

The equations to predict the surface tension and dynamic surface tension of aqueous LiBr in the presence of additive have been developed by Cheng et al. [1] based on a modified kinetic controlled adsorption model as follows, respectively.

$$\sigma = \frac{1}{1 + aX_1 + bX_g} \sigma_0 + \frac{aX_1 + bX_g}{1 + aX_1 + bX_g} \sigma_c \quad (1)$$

$$\sigma_t = \sigma_0 - (\sigma_0 - \sigma_c)[1 - e^{-(kt)^n}] \quad (2)$$

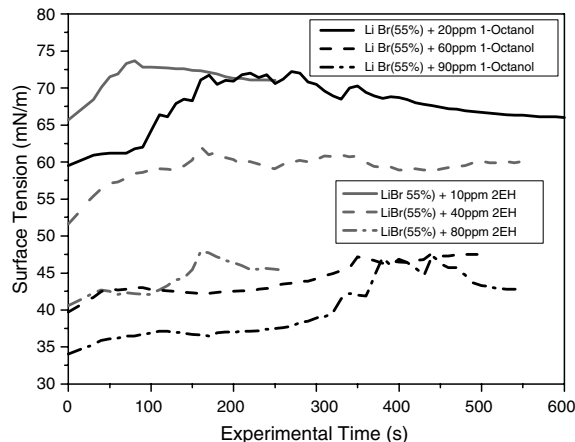


Fig. 1. Oscillations of surface tension of LiBr with additive.

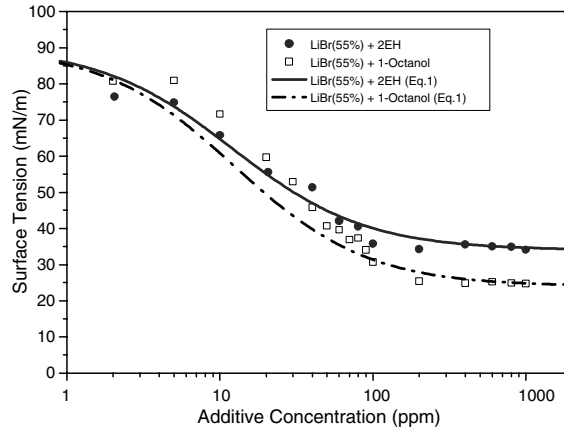


Fig. 2. Surface tension of LiBr with additives.

where, σ_c is the critical surface tension which remains unchanged with change of additive concentration. Both of the coefficients a and b express the potential ability of surface tropism and approach to constants for an isothermal system. The exponent n introduced to Eq. (2), is defined as delay coefficient of dynamic surface tension, and approximates to a constant $n \approx 0.5$ for all cases.

The comparisons between the experimental data of aqueous LiBr with additives 2EH and 1-octanol and the theoretical results were shown in Fig. 2.

3. Experiments

3.1. Experimental apparatus

The experimental apparatus shown in Fig. 3 consists of a test section, a solution tank containing strong LiBr solution, a solution recovery tank, a sampling bottle, an evaporator containing water, a cooling water tank and a vacuum pump. The test section consists of two concentric tubes and serves as a vertical falling film absorber. The outer tube with an outer diameter of 90 mm and thickness of 5 mm, is made of acrylic glass. The inner tube made of stainless steel, is the absorption tube with outer diameter of 15.88 mm and thickness of 1 mm, inside which is for circulating cooling water. The effective length of the absorption tube, defined as the length over which absorption takes place, is 1 m. The cooling water temperature at the test section inlet is controlled in the thermostatic-control unit.

Experiments were performed according to the following procedure. The test section was vacuumed by the vacuum pump. The cooling water circulation was started at a desired flow rate and the temperature controller was turned on to control the temperature of cooling water at the absorber inlet. The LiBr solution with or without additive at the desired flow rate was fed into the test section, and formed a falling film along the vertical absorber. At steady state of the falling film, the valve between the absorber and the evaporator was opened for supplying water vapor to the absorber, and the absorption started. At the end of absorption, the solution samples at the sampling port were taken for mass fraction measurement.

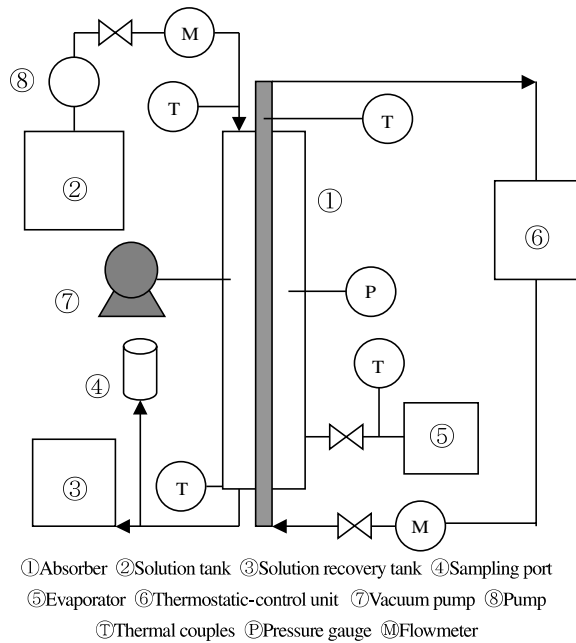


Fig. 3. Experimental apparatus.

Table 1
Experimental conditions

Test section	Pressure [kPa]	0.9
Solution at the inlet	Concentration [wt%]	60 ± 0.5
	Temperature [°C]	40 ± 1.0
	Reynolds number [-]	40–120
Cooling water	Temperature at inlet [°C]	30
	Flow rate [kg/min]	1.2
Additives	Concentration [ppm]	5, 10, 30, 50, 100

In the experiments, the pressure at the test section, the concentration and temperature of LiBr solution at the inlet, and the flow rate and temperature of cooling water at the inlet were kept unchanged. The additive added in the strong aqueous LiBr was 2EH, and 1-octanol respectively. The conditions of the experiment were listed in Table 1.

3.2. Experimental results

The overall heat transfer coefficient U of the absorber is calculated as

$$UA = \frac{Q}{\Delta T_m} \quad (3)$$

where, the total absorber heat transfer rate Q is calculated from the energy transferred to the cooling water,

$$Q = m_{cw}c_{cw}(T_{cw,o} - T_{cw,i}) \tag{4}$$

and the logarithm mean temperature ΔT_m is obtained as

$$\Delta T_m = \frac{(T_i - T_{cw,o}) - (T_o - T_{cw,i})}{\ln [(T_i - T_{cw,o}) / (T_o - T_{cw,i})]} \tag{5}$$

At the same time, the overall heat transfer coefficient can be obtained by,

$$\frac{1}{hA_o} = \frac{1}{UA} - \frac{1}{h_{cw}A_i} - \frac{\ln(d_o/d_i)}{2\pi k_s L} \tag{6}$$

The heat transfer coefficient on the cooling water side and the properties of the tube materials are known. The heat transfer coefficient on the absorption side h can be calculated by Eq. (6). Therefore, the performance characteristic of heat transfer during the absorption process is expressed by Nusselt number,

$$Nu = \frac{h}{\alpha} (v^2/g)^{1/3} \tag{7}$$

The effect of additive 2EH and 1-octanol on absorption was studied respectively. Figs. 4 and 5 showed the effect of additive concentration in aqueous LiBr on the Nusselt number of falling film absorption at $Re = 40$ and 120, respectively. There was an increase of about 100% in the Nusselt number when the additive concentration from 0 ppm to a certain concentration (about 40 ppm) for additives 2EH and 1-octanol at $Re = 40$ and 120. However, the Nusselt number appeared to decrease with the additive concentration thereafter.

The effect of Reynolds number was studied at an additive concentration of 100 ppm for both of 2EH and 1-octanol, and the experimental results were shown in Fig. 6. The Nusselt number decreased as the Reynolds number increased from 40 to 100, and then decreased thereafter.

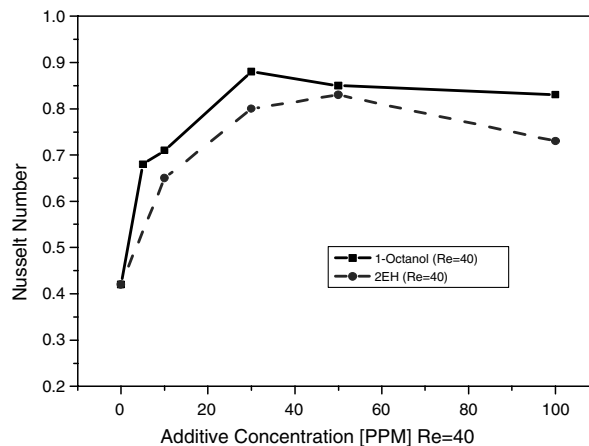


Fig. 4. Effect of additive concentration at $Re = 40$.

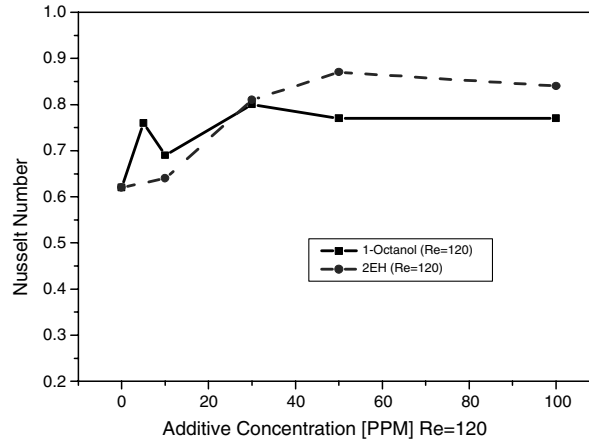
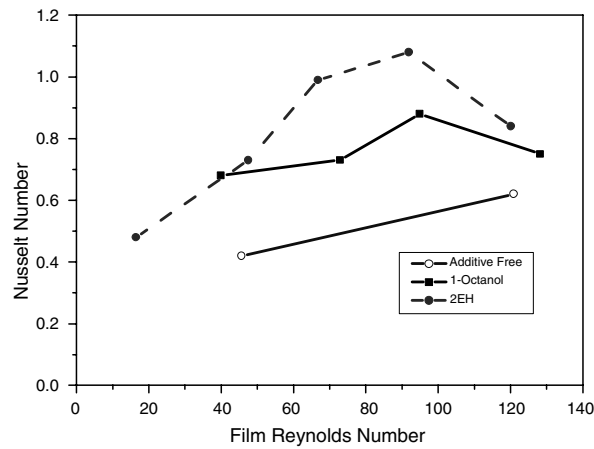
Fig. 5. Effect of additive concentration at $Re = 120$.

Fig. 6. Effect of Reynolds number.

4. Enhancement factor

4.1. Governing equations and boundary conditions

Comparing with the diameter of vertical absorption tube in the experiment, the thickness of the falling film is very small. The governing equations for the heat and mass transfer in the vertical falling film absorption can be written in 2D Cartesian coordinates. Coordinates z and y are the coordinate in the direction of gravity and coordinate perpendicular to the tube respectively, and the origin of y is placed at the free surface of the primary flow (shown in Fig. 7).

The basic equations for the problem are the equation of continuity:

$$\nabla \cdot \mathbf{u} = 0 \quad (8)$$

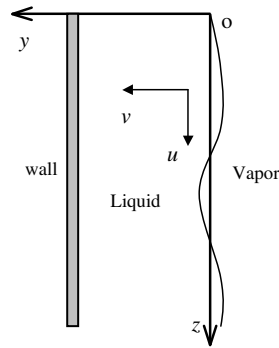


Fig. 7. Schematic diagram of absorption.

the incompressible Navier–Stokes equation:

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{u} + \mathbf{g} \tag{9}$$

the energy equation:

$$\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T = \frac{k}{\rho c} \nabla^2 T \tag{10}$$

and the convection diffusion equation for water and the surface-active solute, respectively

$$\frac{\partial X_w}{\partial t} + \mathbf{u} \cdot \nabla X_w = D_w \nabla^2 X_w \tag{11}$$

$$\frac{\partial X_A}{\partial t} + \mathbf{u} \cdot \nabla X_A = D_A \nabla^2 X_A \tag{12}$$

The liquid–vapor-interface can be expressed as $y = \eta(t, z)$. The kinematic condition, the normal stress balance, and the tangential stress balance in the liquid–vapor-interface boundary may be described as follows, respectively.

$$v = \frac{\partial \eta}{\partial t} + u \frac{\partial \eta}{\partial z} \tag{13}$$

$$p - p_g - 2\mu \left[\frac{\partial v}{\partial y} - \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial z} \right) \frac{\partial \eta}{\partial z} \right] - \sigma \left(\frac{\partial^2 \eta}{\partial z^2} \right) = 0 \tag{14}$$

$$2\mu \left(\frac{\partial v}{\partial y} - \frac{\partial u}{\partial z} \right) \frac{\partial \eta}{\partial z} + \mu \left(\frac{\partial v}{\partial z} + \frac{\partial u}{\partial y} \right) + \left(\frac{\partial \sigma}{\partial z} + \frac{\partial \eta}{\partial z} \frac{\partial \sigma}{\partial y} \right) = 0 \tag{15}$$

Two assumptions are made as (1) the concentration of the additive in the vapor side is zero, and (2) the absorption interface is in equilibrium state. According to the linear absorbent assumption provided by Grossman [3], the absorbent concentration and temperature at a given pressure are related linearly.

$$X_w = -\frac{X_{w,e} - X_{w,i}}{T_e - T_i} T + \frac{X_{w,e} T_e - X_{w,i} T_i}{T_e - T_i} \quad (16)$$

The surface tension contained in Eq. (15) depends on the concentration of water, the concentration of the additive and the temperature, i.e., $\sigma = \sigma(X_w, X_A, T)$. Using the linear absorbent Eq. (16), yields [8]

$$d\sigma = \left(\frac{d\sigma}{dX_w} \right)_i dX_w + \left(\frac{\partial\sigma}{\partial X_A} \right)_i dX_A \quad (17)$$

with

$$\left(\frac{d\sigma}{dX_w} \right)_i = \left(\frac{\partial\sigma}{\partial X_w} \right)_i - \frac{T_e - T_i}{X_{w,e} - X_{w,i}} \left(\frac{\partial\sigma}{\partial T} \right)_i$$

Substitution of Eq. (17) into Eq. (15), gives

$$2\mu \left(\frac{\partial v}{\partial y} - \frac{\partial u}{\partial z} \right) \frac{\partial \eta}{\partial z} + \mu \left(\frac{\partial v}{\partial z} + \frac{\partial u}{\partial y} \right) + \left(\frac{d\sigma}{dX_w} \right)_i \left(\frac{\partial X_w}{\partial z} + \frac{\partial \eta}{\partial z} \frac{\partial X_w}{\partial y} \right) + \left(\frac{\partial\sigma}{\partial X_A} \right)_i \left(\frac{\partial X_A}{\partial z} + \frac{\partial \eta}{\partial z} \frac{\partial X_A}{\partial y} \right) = 0 \quad (18)$$

Assuming that the absorption heat transferred into the vapor phase may be neglected, the heat balance at the interface is obtained as

$$k \left(\frac{\partial T}{\partial y} - \frac{\partial \eta}{\partial z} \frac{\partial T}{\partial z} \right) = \lambda D_w \left(\frac{\partial X_w}{\partial y} - \frac{\partial \eta}{\partial z} \frac{\partial X_w}{\partial z} \right) \quad (19)$$

Considering the diffusion of the additive to the interface from the liquid side, the surface convection of additive at the interface and the surface renewable effect of additive at the interface, the mass balance for the additive in the interface is written as follows,

$$D_A \left(\frac{\partial X_A}{\partial y} - \frac{\partial \eta}{\partial z} \frac{\partial X_A}{\partial z} \right) = \left[\frac{\partial(\Gamma u)}{\partial z} + \frac{\partial \eta}{\partial z} \frac{\partial(\Gamma u)}{\partial y} \right] + \frac{1}{\rho} \frac{\partial \Gamma}{\partial t} \quad (20)$$

Both desorption of the additive to the vapor phase [12] and surface diffusion [8] are assumed negligible in this study.

At the wall ($y = \delta$), zero flow, zero penetration are taken,

$$u = 0, \quad v = 0, \quad \frac{\partial X_w}{\partial y} = 0, \quad \frac{\partial X_A}{\partial y} = 0 \quad (21)$$

and the heat balance at the wall is expressed as the following,

$$k \frac{\partial T}{\partial y} = -h_c (T_w - T_c) \quad (22)$$

4.2. Perturbation analysis

It is assumed that there is a parabolic velocity profile in the y direction of the falling film [8]:

$$U(y) = U_m \left(1 - \frac{y^2}{\delta^2} \right) \quad (23)$$

where, $U_m = g\delta^2/2\nu$. The average velocity U_a can be expressed as:

$$U_a = \int_0^\delta U(y) dy = \frac{2}{3} U_m \quad (24)$$

To simplify the governing equations, the dimensionless variables are defined as follows: $(z^*, y^*) = (z, y)/\delta$, $(u^*, v^*) = (u, v)/U_m$, $p^* = p/(\rho U_m^2)$, $t^* = t/(\delta/U_m)$, $X_w^* = (X_w - X_{w,i})/(X_{w,e} - X_{w,i})$, $X_A^* = X_A/X_{A,i}$, $T^* = (T - T_i)/(T_e - T_i)$. Where the variables with asterisk are dimensionless ones. A small perturbation analysis is carried out based on the governing equations and the boundary conditions. The dimensionless variables are divided into unperturbed values marked by a subscript “s” and infinitesimal perturbations marked by a superscript “’”. $(u^*, v^*) = (u_s, v_s) + (u' + v')$, $p^* = p_s + p'$, $X_w^* = X_{w,s} + X_w'$, $X_A^* = X_{A,s} + X_A'$, $T^* = T_s + T'$, $\Gamma = \Gamma_s + \Gamma'$.

Substituting the dimensionless variables represented by the unperturbed value and the perturbation into Eqs. (8)–(22), the derivation of the linearized perturbation of the governing equations and the boundary equations are obtained. The unperturbed parts of the derivation can be written as:

$$u_s = U(y^*) = U_m(1 - y^{*2}), \quad v_s = 0 \quad (25)$$

$$U \frac{\partial T_s}{\partial z^*} = \frac{3}{2Re \cdot Pr} \left(\frac{\partial^2 T_s}{\partial z^{*2}} + \frac{\partial^2 T_s}{\partial y^{*2}} \right) \quad (26)$$

$$U \frac{\partial X_{w,s}}{\partial z^*} = \frac{3}{2Re \cdot Sc_w} \left(\frac{\partial^2 X_{w,s}}{\partial z^{*2}} + \frac{\partial^2 X_{w,s}}{\partial y^{*2}} \right) \quad (27)$$

$$U \frac{\partial X_{A,s}}{\partial z^*} = \frac{3}{2Re \cdot Sc_A} \left(\frac{\partial^2 X_{A,s}}{\partial z^{*2}} + \frac{\partial^2 X_{A,s}}{\partial y^{*2}} \right) \quad (28)$$

with the unperturbed conditions at the interface ($y = 0$)

$$X_w = 1 - T, \quad \frac{\partial T_s}{\partial y^*} = E \frac{\partial X_{w,s}}{\partial y^*}, \quad \frac{\partial X_{A,s}}{\partial y^{*2}} = Bi_A X_{A,s} \quad (29)$$

and the unperturbed conditions at the wall ($y = 1$)

$$\frac{\partial X_{w,s}}{\partial y^*} = 0, \quad \frac{\partial T_s}{\partial y^*} = -Bi_c(T_w - T_c) \quad (30)$$

These dimensionless parameters appeared in the above equations are defined as:

$$Re = \frac{U_a \delta}{\nu} = \frac{2U_m \delta}{3\nu}, \quad Sc_w = \frac{\nu}{D_w}, \quad Sc_A = \frac{\nu}{D_A}, \quad Pr = \frac{\rho c \nu}{k_c}, \quad Bi_c = \frac{h_c \delta}{k}, \quad E = \frac{\lambda D_w (X_{w,e} - X_{w,i})}{k(T_e - T_i)}$$

where, absorption number E is a normalized heat of the absorption, which represents a ratio of the heat released the interface during absorption of water vapor, to the heat conducted into the aqueous LiBr solution.

The dimensionless perturbation equations where the quadratic terms in the perturbation quantities have been neglected may be obtained:

$$\frac{\partial u'}{\partial z^*} + \frac{\partial v'}{\partial y^*} = 0 \quad (31)$$

$$\frac{\partial u'}{\partial t^*} + U \frac{\partial u'}{\partial z^*} + v' \frac{\partial U}{\partial y^*} = -\frac{\partial p'}{\partial z^*} + \frac{3}{2Re} \left(\frac{\partial^2 u'}{\partial z^{*2}} + \frac{\partial^2 u'}{\partial y^{*2}} \right) \quad (32)$$

$$\frac{\partial v'}{\partial t^*} + U \frac{\partial v'}{\partial z^*} = -\frac{\partial p'}{\partial y^*} + \frac{3}{2Re} \left(\frac{\partial^2 v'}{\partial z^{*2}} + \frac{\partial^2 v'}{\partial y^{*2}} \right) \quad (33)$$

$$\frac{\partial T'}{\partial t^*} + U \frac{\partial T'}{\partial z^*} + v' \frac{\partial T_s}{\partial y^*} = \frac{3}{2Re \cdot Pr} \left(\frac{\partial^2 T'}{\partial z^{*2}} + \frac{\partial^2 T'}{\partial y^{*2}} \right) \quad (34)$$

$$\frac{\partial X'_w}{\partial t^*} + U \frac{\partial X'_w}{\partial z^*} + v' \frac{\partial X_{w,s}}{\partial y^*} = \frac{3}{2Re \cdot Sc_w} \left(\frac{\partial^2 X'_w}{\partial z^{*2}} + \frac{\partial^2 X'_w}{\partial y^{*2}} \right) \quad (35)$$

$$\frac{\partial X'_A}{\partial t^*} + U \frac{\partial X'_A}{\partial z^*} + v' \frac{\partial X_{A,s}}{\partial y^*} = \frac{3}{2Re \cdot Sc_A} \left(\frac{\partial^2 X'_A}{\partial z^{*2}} + \frac{\partial^2 X'_A}{\partial y^{*2}} \right) \quad (36)$$

with the perturbation conditions at the interface ($y = 0$):

$$v' = \frac{\partial \eta}{\partial t^*} + U \frac{\partial \eta}{\partial z^*} \quad (37)$$

$$p' - \frac{3}{Re} \frac{\partial v'}{\partial y^*} - \frac{3}{2Re \cdot Cr} \frac{\partial^2 \eta}{\partial z^{*2}} = 0 \quad (38)$$

$$\frac{\partial v'}{\partial z^*} + \frac{d^2 U}{dy^{*2}} \eta + \frac{\partial u'}{\partial y^*} + Ma \left(\frac{\partial X'_w}{\partial z^*} + \frac{\partial \eta}{\partial z^*} \frac{\partial X_{w,s}}{\partial y^*} \right) - Ma_A \left(\frac{\partial X'_A}{\partial z^*} + \frac{\partial \eta}{\partial z^*} \frac{\partial X_{A,s}}{\partial y^*} \right) = 0 \quad (39)$$

$$X'_w = -T' - \left(\frac{\partial T_s}{\partial y^*} + \frac{\partial X_{w,s}}{\partial y^*} \right) \eta \quad (40)$$

$$\frac{\partial T'}{\partial y^*} = E \frac{\partial X'_w}{\partial y^*} + \left(E \frac{\partial^2 X_{w,s}}{\partial y^{*2}} - \frac{\partial^2 T_s}{\partial y^{*2}} \right) \eta \quad (41)$$

$$\frac{\partial X'_A}{\partial y^*} = -\frac{\partial^2 X_{A,s}}{\partial y^{*2}} \eta + \Pi \frac{\partial u'}{\partial z^*} + Rn \quad (42)$$

Because the perturbation of the variables at the wall and the cooling water, caused by the additive, can be neglected [8], the perturbation conditions at the wall ($y = 1$) are obtained,

$$u' = 0, \quad v' = 0, \quad \frac{\partial X'_w}{\partial y^*} = 0, \quad \frac{\partial X'_A}{\partial y^*} = 0, \quad \frac{\partial T'}{\partial y^*} = 0 \quad (43)$$

In the perturbation equations, the dimensionless parameters, Cr , Π , Ma , and Ma_A defined by [8], are expressed as follows:

$$Cr = \frac{\mu U_m}{\sigma} \tag{44}$$

$$\Pi = \frac{\Gamma_s U_m}{X_{A,0} D_A} \tag{45}$$

$$Ma = \frac{(d\sigma/dX_w)_i (X_{w,e} - X_{w,i})}{\mu U_m} = \frac{(X_{w,e} - X_{w,i})}{\mu U_m} \left(\frac{d\sigma}{dX_w} \right)_i \tag{46}$$

$$Ma_A = - \frac{(\partial\sigma/\partial X_A)_i X_{A,i}}{\mu U_m} \tag{47}$$

According to the surface renewal at the interface caused by the additive during absorption process, a new dimensionless parameter, named renewable number Rn , is defined in this paper as follows:

$$Rn = \frac{\delta}{X_{A,i} \rho D_A} \frac{\partial \Gamma_s}{\partial t} \tag{48}$$

4.3. Enhancement factor

The enhancement effect of additive on the absorption can be expressed by an enhancement factor α_{Nu} , which is defined as the following equation,

$$\alpha_{Nu} = (Nu - Nu_0)/Nu_0 \tag{49}$$

where, Nu is the Nusselt number during the absorption with additive, and Nu_0 is the base Nusselt number during the absorption without additive. The unperturbed equations contribute to the enhancement factor obviously, however the enhancement factor is determined by the perturbation equations of the absorption mainly.

Based on the governing equations and the boundary conditions, the enhancement factor is expressed as

$$\alpha_{Nu} = f(Re, Ma, Ma_A, Rn, \Pi, Cr, Pr, E, Bi_c, Bi_A, Sc_w, Sc_A) \tag{50}$$

Assumed that the enhancement factor can be expressed as the exponential format of the dimensionless parameters and the effect of the Schmidt numbers on the Nusselt number can be neglected [4], the enhancement factor is written by the following equation.

$$\alpha_{Nu} = C Re^e Ma^p Ma_A^r \Pi^n Cr^q Rn^l E^s Bi_c^g Bi_A^h \tag{51}$$

To simplify Eq. (51), a further assumption is made that the enhancement factor is determined by the Reynolds number Re , the surface Marangoni number Ma , the surfactant Marangoni Number Ma_A , the adsorption number Π and the renewable number Rn mainly.

$$\alpha_{Nu} = C Re^e Ma^p Ma_A^r \Pi^g Rn^l \tag{52}$$

In the above equation, the coefficient C and the exponents e, p, r, g, l can be fitted by the experimental results.

According to Eq. (1), the differentiation of the surface tension to the additive concentration in the solution is obtained,

$$\frac{\partial \sigma}{\partial X_A} = \frac{-a}{(1+aX_A)^2} \sigma_0 + \frac{a}{(1+aX_A)^2} \sigma_c = -\frac{a}{(1+aX_A)^2} (\sigma_0 - \sigma_c) \quad (53)$$

Substitution of Eq. (53) into the definition of the surfactant Marangoni number, yields,

$$Ma_A = -\frac{(\partial \sigma / \partial X_A) X_A}{\mu U_m} = -\frac{1}{\mu U_m} \frac{a X_A}{(1+aX_A)^2} (\sigma_0 - \sigma_c) \quad (54)$$

Cheng and et al. [1] provided a linear hypothesis as follows,

$$\sigma = \frac{\Gamma}{\Gamma_c} \sigma_c + \left(1 - \frac{\Gamma}{\Gamma_c}\right) \sigma_0 \quad (55)$$

where, Γ_c is the critical surface concentration defined by Cheng et al. [1]. The following equation will be obtained from Eq. (55):

$$\frac{\partial \Gamma}{\partial t} = -\frac{\Gamma_c}{\sigma_0 - \sigma_c} \frac{\partial \sigma}{\partial t} \quad (56)$$

Based on the dynamic surface tension of Eq. (2), yields,

$$\sigma_t = \sigma_0 - (\sigma_0 - \sigma_e) \left[1 - e^{-(kt)^{0.5}}\right] \approx \sigma_0 - (\sigma_0 - \sigma_e)(kt)^{0.5} \quad (57)$$

Combining Eqs. (56) and (57), we have,

$$\frac{\partial \Gamma}{\partial t} = -\frac{\Gamma_c}{\sigma_0 - \sigma_c} \frac{\partial \sigma}{\partial t} = 0.5k^{0.5} \Gamma_c \frac{aX_A}{1+aX_A} t^{-0.5} \quad (58)$$

Therefore, the surface renewable number Rn is expressed as,

$$Rn = \frac{\delta}{X_{A,i} \rho D_A} \frac{\partial \Gamma_s}{\partial t} = \frac{0.5 \Gamma_c \delta}{\rho D_A} \frac{ak^{0.5}}{1+aX_A} t^{-0.5} \quad (59)$$

Here, the surface renewable number Rn changes with the surface age t . It is obvious that near to the inlet, the surface age is younger, then the surface renewable number Rn is larger, and the Marangoni convection is more vigorous. However, it is focused on the average performance of the enhancement effect caused by additive in this paper. Therefore, the average Rn is calculated by

$$\overline{Rn} = \frac{1}{\Delta t} \int_0^{\Delta t} Rn dt = \frac{\delta \Gamma_c}{\rho D_A} \left(\frac{3L}{2U_m}\right)^{0.5} \frac{ak^{0.5}}{1+aX_A} \quad (60)$$

The surface concentration Γ_s can be expressed as $\Gamma_s = \Gamma_c \frac{aX_A}{1+aX_A}$ [1]. Therefore, the adsorption number is written as

$$\Pi = \frac{\Gamma_s U_m}{X_{A,o} D_A} = \frac{U_m \Gamma_c}{D_A} \frac{a}{1+aX_A} \quad (61)$$

Substituting Eqs. (46), (54), (60) and (61) into Eq. (52), the enhancement factor is rewritten,

$$\alpha_{Nu} = Cf Re^e \left[\left(\frac{d\sigma}{dX_w} \right)_i \right]^p \left[\frac{aX_A(\sigma_0 - \sigma_c)}{(1 + aX_A)^2} \right]^r \left(\frac{a}{1 + aX_A} \right)^g \left(\frac{ak^{0.5}}{1 + aX_A} \right)^l \tag{62}$$

where,

$$f = C \left[\frac{(X_{w,e} - X_{w,i})}{\mu U_m} \right]^p \left(\frac{1}{\mu U_m} \right)^r \left(\frac{U_m \Gamma_c}{D_A} \right)^g \left[\frac{\delta \Gamma_c}{\rho D_A} \left(\frac{3L}{2U_m} \right)^{0.5} \right]^l$$

5. Discussion

Combining the coefficient C and the function f in Eq. (62) into a new coefficient C'' , we have the enhancement factor equation,

$$\alpha_{Nu} = C'' Re^{m''} \left[\left(\frac{d\sigma}{dX_w} \right)_i \right]^p \left[\frac{aX_A(\sigma_0 - \sigma_c)}{(1 + aX_A)^2} \right]^r \left(\frac{a}{1 + aX_A} \right)^g \left(\frac{ak^{0.5}}{1 + aX_A} \right)^l \tag{63}$$

Obviously, the enhancement factor is determined by the parameters related to surface tension and dynamic surface tension, but the experimental data of surface tension are far from sufficient, with the result that these parameters cannot be obtained from experiments accurately. In order to check Eq. (63), the parameters related to surface tension in Eq. (63) are evaluated by the limited experimental data provided by the authors, which are listed in Table 2.

The coefficient and exponents C'' , p , r , g , l are fitted by the least square method from the experimental results provided in Figs. 4 and 5 respectively, then the average values are obtained from the both fitted results. The exponents m'' is fitted from the experimental results provided in Fig. 6. This coefficient and the exponents are listed in Table 3.

From Table 3, it may be found that the exponents of Ma , Ma_A and Rn are positive, however the exponents of II and Re are negative. Therefore, the parameters Ma , Ma_A and Rn will strengthen the enhancement effect of additive on the absorption, but the parameters II and Re will weaken the enhancement effect of additive. On the other words, larger values of $d\sigma/dX_w$, $\sigma_0 - \sigma_c$ and k result in

Table 2
Parameters of surface tension

Additive	$a^{(1)}$	$k^{(2)}$ [s ⁻¹]	$\sigma_0 - \sigma_c$ [mN/m]	$\partial\sigma_c/\partial X_w^{(3)}$ [mN/m]
1-octanol	8.0×10^4	1.30×10^{-5}	69.4	0.45
2EH	8.3×10^4	0.67×10^{-5}	59.4	0.80

Note: (1) a is evaluated by Eq. (1) from the experimental results by the authors. (2) k is evaluated by Eq. (2) from the experimental results presented by [13]. (3) is evaluated from the experimental results presented by [6].

Table 3
The coefficient and exponent in Eq. (63)

C''	m''	p	r	g	l
5.1	-1.03	1.7	2.7	-3.8	1.9

a stronger enhancement effect of additive, however the Reynolds number Re and the surface concentration of additive adsorbed to the interface resist the enhancement effect of additive.

The relationships of the enhancement factor α_{Nu} and the additive concentration in the solution at $Re = 40$ and 120 , are shown in Figs. 8 and 9, respectively. Obviously, there is an optimum additive concentration at which the enhancement caused by the additive is strongest. The optimum concentration is about 40 ppm for both cases of $Re = 40$ and 120 , which agrees well above experimental results.

The relation of enhancement effect and Reynolds number at 100 ppm additive concentration is shown in Fig. 10. It can be found that Eq. (60) agrees well with the experiment results for 1-octanol. However, there is a large difference between Eq. (60) and experimental results for 2-EH, which is caused possibly by that the experiment condition could not be controlled well.

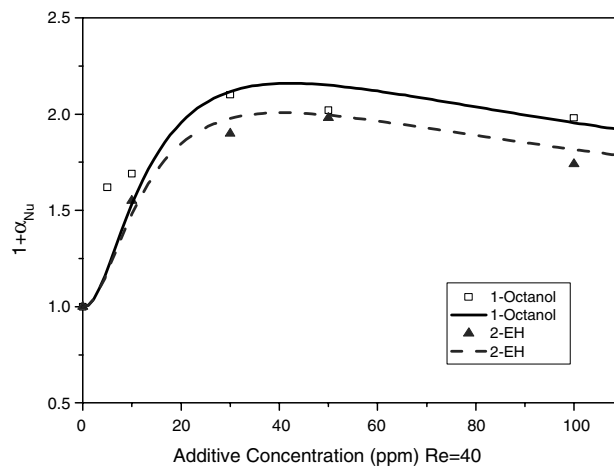


Fig. 8. Relation of α_{Nu} and X_A at $Re = 40$.

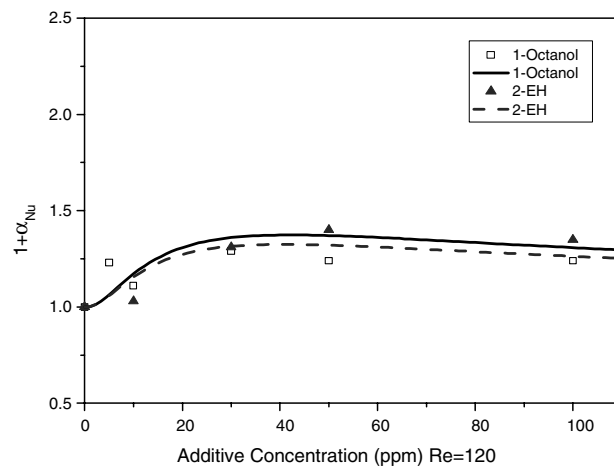


Fig. 9. Relation of α_{Nu} and X_A at $Re = 40$.

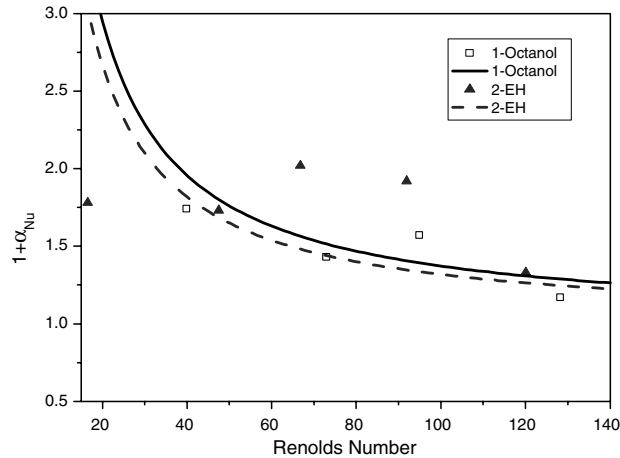


Fig. 10. Relation of α_{Nu} and Re at $X_A = 100$ ppm.

6. Conclusions

The effect of additive on falling film absorption of water vapor into aqueous LiBr was studied by an experimental method. The experimental results showed that small amounts of additive can enhance the heat transfer of absorption process significantly, and the enhancement degree is influenced by additive concentration and Reynolds number. Based on the Navier–Stokes equations of falling film absorption, a new dimensionless parameter, surface renewal number Rn was introduced, and a semi-empirical equation of enhancement factor of additive was obtained, which shows that the enhancement effect of additive on Nusselt number of absorption process is determined by the absorption Marangoni number Ma , the surface Marangoni number Ma_A , the surface renewal number Rn , the adsorption number Π , and the Reynolds number Re . It was proved that the semi-empirical equation can agree with the experimental results well by introduction of the parameters related to surface tension into the equation.

According to the semi-empirical equation, the following conclusions may be obtained:

- (1) There is an optimum additive concentration in which the enhancement effect of additive is strongest.
- (2) The Marangoni number Ma , the surface Marangoni number Ma_A , and the surface renewal number Rn enlarge the enhancement of the heat transfer during absorption.
- (3) The adsorption number Π reduces the heat transfer of absorption.
- (4) The enhancement factor decreases as the Reynolds number increases.

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