

### Pool Boiling Heat Transfer to Alkanolamine Solutions

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#### **Abstract**

Boiling of pure components has been well discussed in the literature, while the boiling of solutions has been studied in less detail due to its high complexity. In this investigation, a large number of experiments have been performed to measure the nucleate boiling heat transfer coefficients of water/diethanolamine (DEA) and water/monoethanolamine (MEA) binary solutions. Based on our experimental data, effects of different physical properties such as surface tension, viscosity and density of solutions on nucleate boiling heat transfer coefficients and also on bubble dynamics have been discussed. Furthermore, in this article a new correlation has been developed on the basis of correlation of Stephan and Körner which is known as a successful correlation for the prediction of nucleate boiling heat transfer coefficient of solutions. Comparison of the prediction of new correlation with our experimental data indicates that this modification can significantly improve the performance of Stephan and Körner correlation.

**Keywords:** Boiling heat transfer, MEA, DEA, New correlation

#### Introduction

Pool boiling has long played a significant role in many technological applications due to its superior heat transfer performance. The complexities encountered in the boiling process have stimulated numerous investigators to conduct extensive research in this field. Boiling of pure components has been well established, while the boiling of mixtures has been studied in less detail. Starting from the pioneering paper of Nukiyama [1], widespread data have accumulated from experimental studies dealing with a diverse array of conditions. Regarding to extensive researches we must admit that a complete understanding of boiling is still lacking, even for any simple cases. Nucleate pool boiling of liquid mixtures finds many applications in chemical and petrochemical process industries. Recent interest as working fluids in thermal power plants and refrigeration systems are growing extensively because of their potential to reduce available energy loss in heat exchanges [2]

#### **Experimental Apparatus, procedure and chemicals**

The complete pool boiling apparatus is shown in Fig. 1. The apparatus consists of a cylindrical stainless steel tank containing 38 liters of test liquid and a vertical condenser to condense the evaporated liquid with tap water and recycle it to the pool. The test section is mounted horizontally within the tank. Tank and condenser are heavily insulated to reduce heat losses to the ambient air. The temperature in the tank is regulated by an electronic temperature controller and a variable electrical transformer in conjunction with a band heater covering the complete cylindrical outside surface. The pressure in the apparatus is monitored continuously and a pressure relief valve is installed for safety reasons. The test heater consists of an internally heated

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stainless steel sheathed rod and four stainless steel sheathed thermocouples which are embedded along the circumference of the heater close to the heating surface. A PC-based data acquisition system was used to measure temperatures and heat flux. The power supplied to the test heater could be calculated from the measured current and voltage drop. The average of five readings was used to determine the difference between wall and bulk temperature for each thermocouple. The heat transfer coefficient, h, is calculated from Equation (1):

$$h = \frac{Q}{\left(T_w - T_b\right)_{av}} \tag{1}$$

Initially, test section and tank were cleaned and the system is connected to a vacuum pump. Once the pressure of the system reached approximately 10 kPa, the test solution was introduced. Following this, the tank band heater was switched on and the temperature of the system allowed rising. Once the system was de-aerated it was left at the desired pressure and the corresponding saturation temperature for about three hours to obtain a homogenous condition throughout. Then, the power was supplied to the test heater and kept at a predetermined value. Data acquisition system was switched-on to record temperatures and heat flux. Some runs were repeated later to check the reproducibility of the experiments, which proved to be excellent.

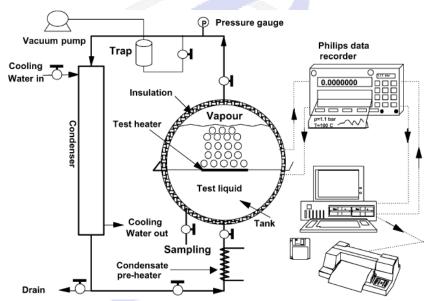


Fig. 1: Schematic diagram of pool boiling apparatus

In this investigation, MEA and DEA individually with distilled water used as test fluids. MEA was prepared from Razi Chemical Complex in Mahshahr in purity greater than 99% by weight and DEA was prepared from Bidboland gas refinery (the first natural gas refinery in Iran) in the purity of 85% by weight. It should be noted that these two chemicals were manufactured in Arak Petrochemical Complex. MEA and DEA are colorless liquids which have slightly ammonia like odor. Fig. 2 shows vapor-liquid equilibrium curves for MEA/water and DEA/water solutions. These were obtained using Non-random two liquids (NRTL) equation with ideal gas and Henry's law which is known to estimate the activity coefficients of non-ideal multicomponent mixtures with good accuracy. The selected correlations and mixing rules were then used in Aspen Plus to estimate the vapor-liquid equilibrium data of the solutions.

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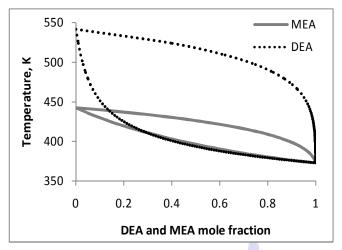


Fig. 2: Bubble point and dew point curves for MEA/water and DEA/water solutions

# **Experimental Results and discussion Results for distilled water**

Distilled water was used to check the accuracy of the experimental results and the calibration of the system for two reasons:

- a) The physical properties of distilled water are well known with high accuracy.
- b) Boiling heat transfer coefficient had been investigated by several investigators over a wide range of heat fluxes and system pressures with highly accurate Gorenflo Standard Pool Boiling Apparatus [3]. All these researches agree that the Gorenflo [3] correlation predict the nucleate pool boiling heat transfer coefficient of distilled water with an absolute, mean and average error of less than 6%.

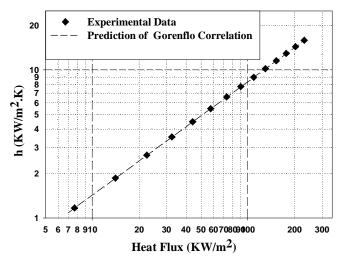


Fig. 3: Pool boiling heat transfer coefficients of distilled water used for calibrating experimental equipment

Fig. 3 illustrates the measured heat transfer coefficient in the present investigation as a function of heat flux at 1 atm (101.3 KPa) pressure. The results illustrate that the heat transfer coefficient increases as heat flux increases. Two distinctive regimes can be distinguished. At low heat fluxes

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- although is not shown here - the heat transfer coefficient depends moderately on heat flux. In this region, heat is transferred mostly by natural convection and is not related to the current investigation. At higher heat fluxes, the increasing wall temperature leads to the formation of bubbles at the surface. In the nucleate boiling regime, the influence of heat flux is stronger and straight line could be fitted through the data points in the double logarithmic plot. The experimental data are compared with the prediction of correlation suggested by Gorenflo [3]. Fig. 3 shows that the experimental results are in good agreement with the values predicted by this correlation.

#### **Results for binary solutions**

Boiling heat transfer coefficients for binary solutions of MEA/water and DEA/water were obtained for various solution concentrations including: 8, 15, 25, 36, 56 and 70 wt% of less volatile components. According to the literature, boiling curves of the liquid mixtures are found to shift to the right hand side, indicating the reduction of heat transfer compared to pure fluids [4, 5]. Fig. 4 and Fig. 5 display the dependency of boiling heat transfer coefficient on composition at four different constant heat fluxes for MEA/water and DEA/water binary solutions, respectively. It is observed that the boiling heat transfer coefficient of liquid mixtures is less in compare to pure liquids.

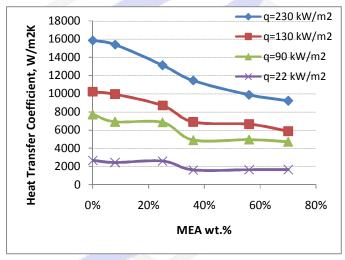


Fig. 4: Heat transfer coefficient of MEA/water binary mixtures against MEA wt.% at four different heat fluxes

In the boiling of pure liquids, the liquid and vapor compositions at the liquid bulk and vapor inside the bubble are the same and consequently the entire boiling process is heat transfer controlled. In contrast, during the boiling of a multicomponent solution, the vapor-liquid phase equilibrium characteristics of the mixture allow the vapor and liquid phases to be at different compositions. Hence, as a liquid mixture evaporates on the heating surface, the vapor contains more of the light component(s). Therefore, the micro-layer is depleted of the light component(s) and enriched in heavy component(s). This results in mass diffusion of the light component(s) from the vapor to the micro-layer. Since the rate of mass diffusion is much slower than heat diffusion, mass transfer of the light component(s) to the bubble interface becomes the limiting process and a portion of the driving force is utilized in overcoming the mass transfer resistance.

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Therefore, to obtain a given heat flux, an additional temperature driving force is required for mixtures in compare to pure liquids.

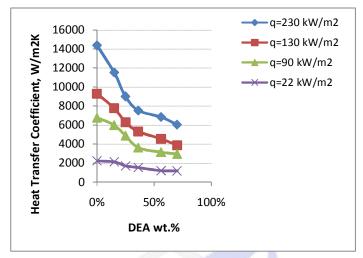
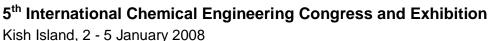


Fig. 5: Heat transfer coefficient of DEA/water binary mixtures against DEA wt.% at four different heat fluxes

Fig. 4 and Fig. 5 also present the addition of amine to distilled water usually causes deterioration in the heat transfer. Thus, the composition is an important factor affecting the heat transfer process during the boiling of binary solutions. As the composition varies, a number of physical properties characterizing the mixture also change, such as the surface tension, density and viscosity of the boiling mixture. Even for the same solution concentrations, heat transfer reduction is not uniform for heat flux variations, with larger reductions occurring at higher heat fluxes as can be seen in Figs. 4 and 5. These two characteristics regarding the influence of composition and heat flux on heat transfer reduction were also observed more or less in other kinds of two-component solutions investigated in the past. This could be related to non-linear variation in the solution physical properties with composition [6].

# Effect of Liquid Properties (a) Viscosity of the Liquid

With the variation in the viscosity of the liquid, the magnitude of viscous forces exerted during bubbles formation changes such that a stable bubble diameter is attained before its detachment. The experimental observations by various investigators have brought different views in this regard. The reported observations in such studies are contradicting viz. (i) the bubble sizes increase with liquid viscosity [7, 8] (ii) bubble sizes are independent of liquid viscosity [9]. Based on the above discussion on the impact of viscosity on heat transfer coefficient, it is obvious from Fig. 8 that the addition of MEA and DEA to water would increase the viscosity of mixture and this result in decreasing heat transfer coefficient. Indeed, most probably viscosity is one of the main reasons which caused large heat transfer reduction in DEA/water binary solutions.





0.95 **DEA** solution 0.85 MEA solution 0.75 Viscosity, cp 0.65 0.55 0.45 0.35 0.25 0 0.2 0.4 0.6 0.8 **DEA and MEA wt. fraction** 

Fig. 6: Viscosity vs. concentration for MEA/water and DEA/water mixtures

#### (b) Surface tension of the Liquid.

In the case of bubble formation at a nucleation site, for a growing bubble, its rear surface is dragged backward along with the liquid. In the front portion of the bubble, the surface is stretched and the new surface is constantly generated. In the portion close to the nucleation site, the bubble surface is compressed and the liquid is pushed toward the edges. As an effect, the surface forces on a bubble arise out of the linear surface tension acting on it and it helps a bubble to adhere to the edge of nucleation site, delaying the detachment process. Two types of surface tension forces act on a bubble, dynamic and static. During the initial part of growth phase, the surface tension is dynamic as its contact angle with the orifice changes continuously and in the later part, it reaches to a constant contact angle approaching to static surface tension, hence surface tension decides the orientation time/growth time for bubbles.

Apparently, the addition of a small amount of MEA and DEA into the water reduces the surface tension of the solution, therefore, coalescence of small embryos into larger bubbles is inhibited, bubble frequency is increased, dryout on the heated surface is reduced, and the critical heat flux condition is delayed [10]. Effect of the addition of DEA and MEA to water on the surface tension of solutions has been presented in Fig. 7.

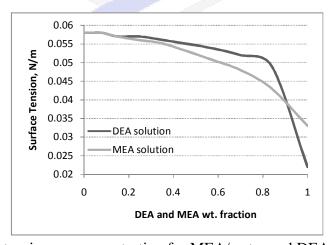


Fig. 7: Surface tension vs. concentration for MEA/water and DEA/water mixtures



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#### (c) Liquid Density

To attain stability, a bubble attains a shape close to a sphere causing an early detachment. It is known that during the formation of a bubble, its pressure energy is equal to the static head above it, i.e., liquid density. The effect of density can be seen from the following two observations: (I) the bubble volume decreases with increase in liquid density and (II) it is independent of liquid density. Rise in the static head leads to the first observation, whereas the second observation should be true for very shallow liquid heads [8].

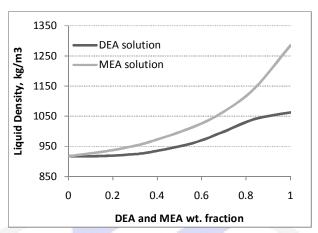


Fig. 8: Liquid density vs. concentration for MEA/water and DEA/water mixtures

#### **Development of new correlation**

In 1969 Stephan and Körner have suggested a simple method whereby heat transfer coefficients in binary systems may be computed from data for the pure components. The method is illustrated in Fig. 9. The upper part of this diagram represents an equilibrium diagram for the system A-B and shows the mole fraction of component B in the vapor phase (y) plotted against the mole fraction of component B in the liquid phase (x) for a constant pressure. The lower part of diagram shows the difference in temperature between the heating surface  $T_w$  and the bubble point  $T_{sat}(x)$  corresponding to a liquid composition (x). The curve of  $(T_w$ -  $T_{sat}(x))$  passes through a maximum corresponding to the maximum value of (y-x). The value of  $(T_w$ -  $T_{sat}(x))$  may be expressed as;

$$(T_w - T_{sat}(x)) = \Delta T_I + \Delta T_E = \Delta T_I (1 + \Theta)$$
(2)

In which,  $\Delta T_I$  is the ideal value of temperature difference and is evaluated from the values of  $\Delta T_{sat}$  for the two pure components A and B calculated for the same pressure and heat flux as the mixture. These wall superheat values will be denoted  $\Delta T_A$  and  $\Delta T_B$ , respectively. Then  $\Delta T_I$  is given by

$$\Delta T_I = (1 - x)\Delta T_A + \Delta T_B \tag{3}$$

Stephan and Körner found that  $\Theta$  in Equation (2) could be correlated against the value of (y-x). Thus:

$$\Theta = A(y - x) \tag{4}$$

"A" was found to vary with pressure, and over the pressure range of 1-10 bar the following expression was used:

$$A = A_o \left( 0.88 + 0.12P \right) \tag{5}$$

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Where "P" is the system pressure in bar and  $A_0$  is a constant dependent on particular binary system studied. Values of  $A_0$  are given in Table 2 for some common systems. A value of  $A_0$  of 1.53 was recommended when no experimental data for the system under consideration are available. This method is not reliable if one of the components is strongly surface active [11].

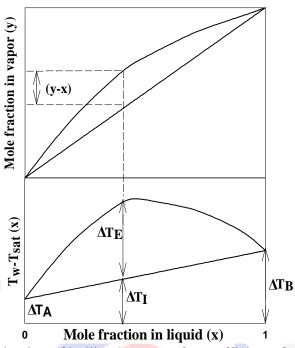


Fig. 9: The evaluation of boiling heat transfer coefficients for binary systems

Table 2: Values of  $A_0$  for use in Equations (4) and (5) for the estimation of nucleate boiling heat transfer coefficients for binary mixtures [11]

System	$A_0$
Acetone-ethanol	0.75
Acetone-butanol	1.18
Acetone-water	1.40
Ethanol-benzene	0.42
Ethanol-cyclohexane	1.31
Ethanol-water	1.21
Benzene-toluene	1.44
Isopropanol-water	2.04
Methyl ethyl keton-toluene	1.32
Methyl ethyl keton-water	1.21
Propanol-water	3.29
Water-glycerine	1.50
Water-pyridin	3.56

All the correlations which were developed on the basis of concentration difference of light component in vapor and liquid phases, (y-x), have an adjustable parameter which should be determined via experiment. In the case of Stephan and Körner correlation, this adjustable

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parameter is  $A_0$ . In order to find the value of this parameter, the following procedures have to be performed.

$$\frac{h}{h_{id.}} = \frac{1}{1 + A_o(y - x)(0.88 + 0.12P)}$$
(6)

In the experiments which are selected for the development of new model total pressure was maintained constant at 1 bar. So, the value of (0.88+0.12P) is equal to unity. Thus:

$$\frac{h}{h_{id.}} - 1 = A_o \left( y - x \right) \tag{7}$$

Now, if we plot the left hand side term in Equation (8) against (y-x) for each heat flux, the slopes of the lines which are fitted by the aid of linear regression give  $A_0$  for each heat flux such as shown in Fig. 10 for MEA/water and DEA/water solutions.

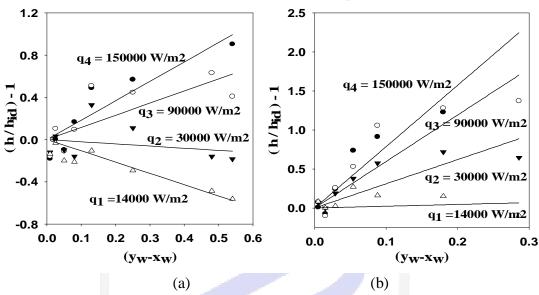


Fig. 10: Plotting (h / hid) - 1 against  $(y_w - x_w)$  in order to find  $A_0$  in Stephan and Körner correlation, a) for MEA/water solutions, b) for DEA/water solutions

Since the value of  $A_0$  in Stephan and Körner correlation varies with heat flux, we can find this dependency by means of plotting  $A_0$  against the heat flux and fitting a line to these points. It was shown in Fig. 11 for MEA/water and DEA/water binary mixtures and the subsequent equations were found for  $A_0$ . Therefore, in the case of MEA/water binary mixtures the correlation of Stephan and Körner modifies to the following form:

$$\frac{h}{h_{id.}} = \frac{1}{1 + (0.0117Q - 0.5894)(0.88 + 0.12P)(y - x)}$$
(8)

And for DEA/water binary mixtures this correlation changes as follow:

$$\frac{h}{h_{id.}} = \frac{1}{1 + (0.0358Q - 1.8463)(0.88 + 0.12P)(y - x)}$$
(9)

Thus, in the new correlation "A" is function of pressure and heat flux simultaneously.



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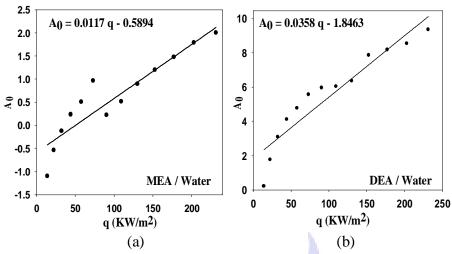


Fig. 11: Variation of  $A_0$  in Stephan and Körner correlation with heat flux a) MEA/water solutions b) DEA/water solutions

#### **Comparison of results**

Nucleate boiling heat transfer coefficient of MEA/water and DEA/water binary mixtures have been compared with the three different states of correlation suggested by Stephan and Körner and the respective RMS error - which is defined as Equation (10) - produced in the prediction of these correlations have been represented in Table 3.

$$E_{Rms} = \left(\frac{1}{n} \sum_{i=1}^{n} \left(\frac{h_{\exp,i} - h_{cal,i}}{h_{\exp,i}}\right)^{2}\right)^{0.5}$$
(10)

Data in Table 3 indicate that when  $A_0$ =1.53, error is greater than others. It was recommended by Stephan and Körner [11] to apply this case when no experimental data are available but in the presence of experimental data if  $A_0$  is considered as a function of heat flux, the respective error is smaller than the case in which  $A_0$  is constant for each binary. It is found that  $A_0$ =1.25 is the best value which minimizes predictive error for MEA/water mixtures and  $A_0$ =7.1 is the best value for DEA/water mixtures. These two values can be added to the Table 2 for these pair of binary mixtures.

Table 3: RMS errors produced by different modifications to Stephan and Körner correlation to predict nucleate boiling heat transfer coefficient of mixtures

Dinary colution	$A_0 = 1.53$	$A_0$ =The best constant	New correlation	Number of experimental
Billary solution			$A_0 = f(q)$	data
MEA/water	23.8 %	23.6 %	18.7 %	101
DEA/water	36.8 %	17.0 %	14.5 %	87

#### Conclusion

The heat transfer to liquid mixtures of water/diethanolamine and water/monoethanolamine were investigated over a wide range of heat flux and concentration under saturated pool boiling condition. The following conclusions were obtained:



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- 1) As a liquid mixture evaporates on the heating surface, the vapor contains more of the light component(s). Therefore, the micro-layer is depleted of the light component(s) and enriched in heavy component(s). This results in mass diffusion of the light component(s) from the bulk to the micro-layer. Since the rate of mass diffusion is much slower than heat diffusion, a portion of the driving force is utilized in overcoming the mass transfer resistance. Therefore, this leads to the degradation of boiling heat transfer coefficients of binary mixtures compare with pure water.
- 2) It is shown that by the addition of MEA and DEA to water, viscosity and density of liquid solutions increased and surface tension of liquid solutions decreased. The effects of these physical properties on the bubble dynamics and heat transfer processes have been demonstrated.
- 3) A new correlation was developed on the basis of Stephan and Körner correlation to predict nucleate boiling heat transfer coefficient of binary mixtures. It was shown that this modification can improve the performance of Stephan and Körner correlation up to 20%.

#### **Notation:**

#### Roman symbols:

 $\Theta$  a term in Eq. (2)

#### Letters:

A Pressure dependent term in Stephan and Korner correlation
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$A_{\it 0}$	Constant in Stephan and Korner correlation	E	Error
h	Heat transfer coefficient (W/m <sup>2</sup> K)	n	number of experimental data
P	Pressure (bar)	Q	Heat flux (W/m <sup>2</sup> )
T	Temperature (K)	$\Delta T$	Temperature difference (K)
X	Liquid phase mole fraction	y	Vapor phase mole fraction

#### Superscripts and subscripts:

Supers	cripis ana savscripis.			
A	component A		В	component B
av.	Average		b	Bulk
cal.	Calculated		E	Excess
exp.	Experimental		id.	Ideal
I	Ideal		Rms	Root of mean square
sat.	saturation		w	wall

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