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The influence of mass transport on the heat transfer coefficients during the boiling of multicomponent mixtures [1]

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Abstract — The paper describes a mathematical model of the process based on multicomponent mass transfer theory which enables the effect to be predicted of mass transport on the boiling heat transfer coefficient. The results of calculations were compared with our own experimental pool boiling data for the ternary system methanol–isopropanol–water and with Grigoriev's data obtained for the system acetone–methanol–water. The good accuracy was obtained when the ratio of the tube surface area to the surface area of the bubbles, which touch the heater at that moment, was considered as a parameter of the model. Based on our own experimental pool boiling data for the system methanol–isopropanol–water and the corresponding binary systems the triangular diagram of the ratio $\alpha_{\mathrm{exp}}/\alpha_{\mathrm{id}}$ as a function of the liquid compositions is presented. © 2000 Éditions scientifiques et médicales Elsevier SAS

boiling / multicomponent mixtures / mass transfer / heat transfer

Nomenclature

B	ratio of the tube surface to the area of bubbles attached to the tube	
$D_{i,j}$	binary diffusion coefficient (i, j)	$\mathrm{m^2 \cdot s^{-1}}$
d_{p}	vapour bubble diameter	m
$\mathbf{E}$	unit matrix	
F	tube surface area	$\mathrm{m^2}$
f	bubble surface area	$\mathrm{m^2}$
ΔH	molar latent heat of vaporization	$\mathrm{J \cdot kmol^{-1}}$
i	number of bubbles	
$\mathbf{K}$	equilibrium constant matrix	
n	number of mixture components	
$\mathbf{N}$	vector of mass fluxes	$\mathrm{kmol \cdot m^{-2} \cdot s^{-1}}$
N_{T}	total mass flux	$\mathrm{kmol \cdot m^{-2} \cdot s^{-1}}$
q	heat flux	$\mathrm{W \cdot m^{-2}}$
Q	heat exchanged	W
T	temperature	K
w	bubble growth rate	$\mathrm{m \cdot s^{-1}}$
$\mathbf{x}$	vector of mole fractions in liquid phase	
$\mathbf{y}$	vector of mole fractions in vapour phase	

Greek symbols

α	heat transfer coefficient	$\mathrm{W \cdot m^{-2} \cdot K^{-1}}$
β	mass transfer coefficient	$\mathrm{kmol \cdot m^{-2} \cdot s^{-1}}$
$\boldsymbol{\beta}$	square matrix of mass transfer coefficients $(n-1) \times (n-1)$	
$\mathbf{\Theta}$	matrix of correction coefficients allowing for finite rates of mass transfer $(n-1) \times (n-1)$	
$\mathbf{\Phi}$	rate factor matrix $(n-1) \times (n-1)$	

Superscripts

$\bullet$	value corrected for large fluxes

Subscripts

calc	calculated value
exp	experimental value
I	refers to interface
w	refers to wall
L	refers to liquid
G	refers to vapour

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1. INTRODUCTION

Processes involving the boiling of multicomponent liquid mixtures are frequently met in a number of industrial applications. Similarly as in binary systems, due to the mass transfer the interfacial liquid composition and temperature differ from those in the bulk liquid. Thus the actual heat transfer coefficients are lower than the mean value estimated based on the individual components.

Most of the experimental works which can be found in literature refer to binary systems. The study of multicomponent mixtures in comparison to binary systems is much more tedious due to the large number of experiments required to cover the whole composition range of all the components. Only few ternary systems were studied experimentally [1–3].

2. EXPERIMENTAL

Our experiments for the ternary system methanol–isopropanol–water were performed in apparatus used for binary systems and described in a previous work [4]. The main part of the apparatus was a cylindrical vessel (evaporator) equipped with an electrically heated horizontal tube ($\varnothing = 16$ mm, $l = 400$ mm). The side-glass covers enable the boiling process to be visualized. The evaporator was equipped with ports for taking samples of liquid and vapour for analysis, manometer, level gauge and four parts in the front cover to measure the temperature of vapour and liquid inside the vessel.

The experimental (actual) values of the heat transfer coefficients α_{exp} were calculated from the heat flux and temperature difference between the mean temperature of the tube surface T_{W} (measured by six thermocouples Ni–Cr–Ni at different radial positions) and the saturation temperature for a given liquid composition T_{S}.

For both the systems studied methanol–isopropanol–water and acetone–methanol–water (see [3] and [1], respectively) the experimental values of heat transfer coefficients α_{exp} are much lower than the ideal coefficient α_{id}, calculated as a weighed harmonic mean of the coefficients estimated for the individual components of the mixture, for q varying from 30 to 240 kW·m^{-2}. On the basis of our own experimental data for the system methanol–isopropanol–water the triangular diagram of the ratio $\alpha_{\text{exp}}/\alpha_{\text{id}}$ as a function of the liquid composition was presented in *figure 1*. *Figure 1* shows that the minimum of $\alpha_{\text{exp}}/\alpha_{\text{id}}$ in the ternary mixture is lower than that for the corresponding binary mixtures. Similar results were obtained by Grigoriev et al. [1] for the system acetone–methanol–water. In contrary to these results, Stephan and Preusser [2] found for the system acetone–methanol–water (the same as [1]) that the reduction in heat transfer coefficients for ternary mixtures was less than that for binary mixtures. These conflicting conclusions were reported earlier by Thome and Shock [5] who suggested more experimental work on ternary systems.

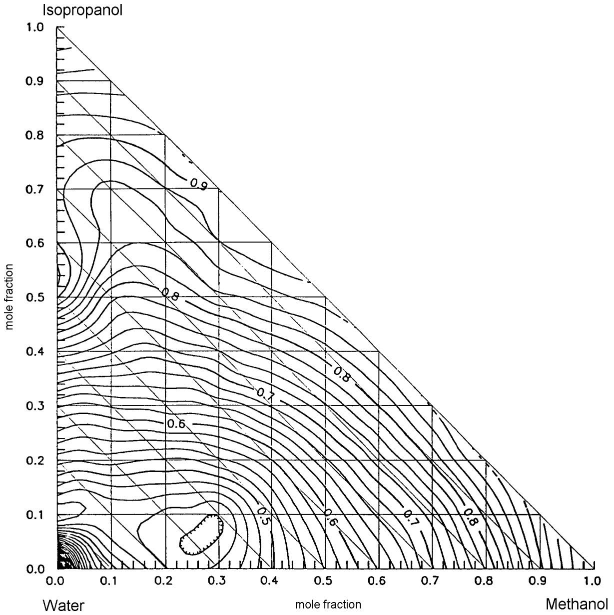

Figure 1. The dependence of the ratio $\alpha_{\text{exp}}/\alpha_{\text{id}}$ on a composition for the ternary system methanol–isopropanol–water ($q = 50$ kW·m^{-2}).

3. MODEL OF THE PROCESS

In most of the published correlations the measured or actual heat transfer coefficients α are based on the difference between the wall and saturation temperatures $(T_{\text{W}} - T_{\text{S}})$. On the other hand the so called ideal heat transfer coefficient is estimated based on the difference between the wall and interfacial temperatures $(T_{\text{W}} - T_{\text{I}})$. Applying the heat flux equations to the two definitions of heat transfer coefficients the fundamental relationship between these coefficients can be obtained in the form [6]

$$\frac{\alpha}{\alpha_{\text{id}}} = \left[1 + \frac{\alpha_{\text{id}}}{q}(T_{\text{I}} - T_{\text{N}})\right]^{-1} \tag{1}$$

During the boiling of multicomponent mixtures, due to the mass transport from the bulk liquid to the bulk of the vapour phase the composition of the mixture varies over a given cross-section. Due to the preferential evaporation of more volatile components their interfacial concentrations are lower than those in the bulk liquid. Therefore, the interfacial temperature T_{I} is higher than the boiling point T_{N} of the liquid of composition $\mathbf{x}^{\mathrm{T}} = (x_1, \ldots, x_n)$. Thus, according to equation (1) for T_{I} higher than T_{N} the actual heat transfer coefficient α should be lower than the ideal coefficient α_{id}. It follows from equation (1) that in order to determine the actual heat transfer coefficients α during the boiling of multicomponent mixtures it is necessary to know the interfacial temperature, which can be evaluated based on the following simplifying assumptions:

- all the heat supplied by the heater is only utilized to generate vapour,
- the vapour and liquid phases are in thermodynamic equilibrium at the interface,
- diffusional resistance appears in the liquid phase or in both of the phases,
- the liquid concentrations $\mathbf{x}^{\mathrm{T}} = (x_1, \ldots, x_n)$ are constant during the bubble formation.

The analysis of the various literature approaches applying the Maxwell–Stefan diffusion equations for an n-component mixture [7–10] has been based on film theory. From a linaerized general model the individual mass fluxes of the components transferring from the liquid to the vapour bulk can be presented in the concise matrix form as

$$\begin{aligned} \mathbf{N} &= \boldsymbol{\beta}^{\bullet}_{\mathrm{L}}(\mathbf{x} - \mathbf{x}_{\mathrm{I}}) + N_{\mathrm{T}}\mathbf{x}_{\mathrm{I}} \\ &= \boldsymbol{\beta}^{\bullet}_{\mathrm{G}}(\mathbf{y}_{\mathrm{I}} - \mathbf{y}) + N_{\mathrm{T}}\mathbf{y}_{\mathrm{I}} \end{aligned} \tag{2}$$

in which $(n-1) \times (n-1)$ matrices of mass transfer coefficients $\boldsymbol{\beta}^{\bullet}_{\mathrm{L}}$ and $\boldsymbol{\beta}^{\bullet}_{\mathrm{G}}$ are defined on the spectrum of corresponding matrices $\mathbf{D}_{\mathrm{L}}$ and $\mathbf{D}_{\mathrm{G}}$. The black dots show that they are corrected for the finite mass-transfer rate. The $\mathbf{x}$, $\mathbf{y}$, $\mathbf{x}_{\mathrm{I}}$ and $\mathbf{y}_{\mathrm{I}}$ are the $(n-1) \times 1$ column matrices of mole fractions in the bulk liquid and vapour phases and at the interface, respectively. The elements of the reciprocal matrix of diffusion coefficients in the vapour phase $\mathbf{D}_{\mathrm{G}}$ are given by

$$\begin{gathered} D^{-1}_{k,k} = \frac{1}{C_{\mathrm{G}}}\left(\frac{y_k}{D_{k,n}} + \sum_{j=1,\, j\neq k}^{n} \frac{y_j}{D_{k,j}}\right) \\ D^{-1}_{k,j} = \frac{y_k}{C_{\mathrm{G}}}\left(\frac{1}{D_{k,n}} - \frac{1}{D_{k,j}}\right) \\ j, k = 1, \ldots, (n-1) \end{gathered} \tag{3}$$

In practical computations the matrix functions $\boldsymbol{\beta}^{\bullet}_{\mathrm{G}}(\mathbf{D}_{\mathrm{G}})$ can be calculated according to Sylvester's theorem [11] on the basis of matrix $\mathbf{D}^{-1}_{\mathrm{G}}$ and its eigenvalues. For the liquid phase the matrix of diffusion coefficients were calculated taking the effect of liquid concentrations on the matrix of diffusivities $\mathbf{D}_{\mathrm{L}}$, according to the relationships given by [12].

According to the assumptions of the model, $\mathbf{y}$ and $\mathbf{x}$ are related by the equilibrium matrix formulae which can be written as

$$\mathbf{y}_{\mathrm{I}} = \mathbf{K}\mathbf{x}_{\mathrm{I}} \tag{4}$$

where $\mathbf{K}$ is a diagonal matrix of the coefficients equal to

$$K_{j,j} = \frac{P^*_j \gamma_j}{\sum_{j=1}^{n} P^*_j \gamma_j x_{j,\mathrm{I}}} \tag{5}$$

Inserting equation (4) into (2) and solving for mole fractions at the interface $\mathbf{x}_{\mathrm{I}}$ we get

$$\begin{aligned} \mathbf{x}_{\mathrm{I}} = {} & \left[\mathbf{E} + N_{\mathrm{T}}\left(\boldsymbol{\beta}^{\bullet}_{\mathrm{L}}\right)^{-1}(\mathbf{K} - \mathbf{E}) + \left(\boldsymbol{\beta}^{\bullet}_{\mathrm{L}}\right)^{-1}\boldsymbol{\beta}^{\bullet}_{\mathrm{G}}\mathbf{K}\right]^{-1} \\ & \cdot \left[\mathbf{x} + \left(\boldsymbol{\beta}^{\bullet}_{\mathrm{L}}\right)^{-1}\boldsymbol{\beta}^{\bullet}_{\mathrm{G}}\mathbf{y}\right] \end{aligned} \tag{6}$$

The matrices of mass transfer coefficients are functions of the total mass flux N_{T} of the boiling mixture, and are defined as follows:

$$\boldsymbol{\beta}^{\bullet}_{\mathrm{L}} = \boldsymbol{\beta}_{\mathrm{L}}\boldsymbol{\Theta}_{\mathrm{L}}, \qquad \boldsymbol{\beta}^{\bullet}_{\mathrm{G}} = \boldsymbol{\beta}_{\mathrm{G}}\boldsymbol{\Theta}_{\mathrm{G}} \tag{7}$$

Assuming that the positive directions of the fluxes are associated with the species leaving the liquid phase, the matrices $\boldsymbol{\Theta}_{\mathrm{L}}$ and $\boldsymbol{\Theta}_{\mathrm{G}}$ according to the film theory are equal to

$$\begin{aligned} \boldsymbol{\Theta}_{\mathrm{L}} &= \boldsymbol{\Phi}_{\mathrm{L}}\left[\mathbf{E} - \exp(-\boldsymbol{\Phi}_{\mathrm{L}})\right]^{-1}; & \boldsymbol{\Phi}_{\mathrm{L}} &= N_{\mathrm{T}}\boldsymbol{\beta}^{-1}_{\mathrm{L}} \\ \boldsymbol{\Theta}_{\mathrm{G}} &= \boldsymbol{\Phi}_{\mathrm{G}}\left[\exp(\boldsymbol{\Phi}_{\mathrm{G}}) - \mathbf{E}\right]^{-1}; & \boldsymbol{\Phi}_{\mathrm{G}} &= N_{\mathrm{T}}\boldsymbol{\beta}^{-1}_{\mathrm{G}} \end{aligned} \tag{8}$$

It can be shown that for $N_{\mathrm{T}} \to \infty$ ($\boldsymbol{\Phi}_{\mathrm{L}} \to \infty$ and $\boldsymbol{\Phi}_{\mathrm{G}} \to \infty$)

$$\mathbf{x} = \mathbf{y}_{\mathrm{I}} = \mathbf{K}\mathbf{x}_{\mathrm{I}} \tag{9}$$

Thus, we get at interesting conclusion: for very large fluxes the vapour composition at the interface becomes equal to that in the bulk liquid since, according to the assumptions of the model, the interfacial temperature T_{I} must be equal to the dew point of the liquid whose composition is equal to the interfacial vapour composition.

If the mass transfer resistance in the vapour phase is neglected, i.e. $\mathbf{y}_{\mathrm{I}}$ is assumed as equal $\mathbf{y}$, then the matrix equation (2) has the following form:

$$\mathbf{N} = \boldsymbol{\beta}^{\bullet}_{\mathrm{L}}(\mathbf{x} - \mathbf{x}_{\mathrm{I}}) + N_{\mathrm{T}}\mathbf{x}_{\mathrm{I}} = N_{\mathrm{T}}\mathbf{y}_{\mathrm{I}} \tag{10}$$

Upon elimination of the interfacial concentration in the vapour phase $\mathbf{y}_\mathrm{I}$ using equation (4), the interfacial concentration in the liquid can be found from equation (10)

$$\mathbf{x}_\mathrm{I} = \left[\mathbf{E}^{-1} + N_\mathrm{T}\left(\boldsymbol{\beta}_\mathrm{L}^{\bullet}\right)^{-1}(\mathbf{K}-\mathbf{E})\right]^{-1}\mathbf{x} \qquad (11)$$

As previously for $N_\mathrm{T} \to \infty$ ($\boldsymbol{\Phi}_\mathrm{L} \to \infty$)

$$\mathbf{x}_\mathrm{I} = \mathbf{K}^{-1}\mathbf{x} \quad \Longrightarrow \quad \mathbf{y}_\mathrm{I} = \mathbf{x} \qquad (12)$$

The vapour phase interfacial concentration $\mathbf{y}_\mathrm{I}$ is equal to the bulk liquid concentrations and these conditions correspond to the dew point (T_D). In this case the ratio $\alpha/\alpha_\mathrm{id}$, equation (1), reaches its minimum.

For small mass fluxes at $N_\mathrm{T} \to 0$ and $\boldsymbol{\Phi}_\mathrm{L} = N_\mathrm{T}\boldsymbol{\beta}_\mathrm{L}^{-1} \to 0$

$$\mathbf{x}_\mathrm{I} = \mathbf{x} \qquad (13)$$

This means that the interfacial liquid temperature T_I is equal to the saturation temperature T_N, and the ratio $\alpha/\alpha_\mathrm{id}$, equation (1), is equal to unity.

To solve the model equations (6) and (11) it is necessary to determine the total mass flux N_T. If we assume (according to the model's assumption) that, at a given moment, all the heat supplied by the heater surface, F, is utilized to generate vapour bubbles which touch the heater at that moment and have the area fi, then the total flux, N_T, can be estimated from the heat balance

$$Q = Fq = fi\,\Delta H\,N_\mathrm{T} \qquad (14)$$

Denoting the ratio of the tube surface area to the bubble surface area by

$$\frac{F}{fi} = B \qquad (15)$$

the total mass flux N_T can be calculated as

$$N_\mathrm{T} = \frac{qB}{\Delta H} \qquad (16)$$

Due to the experimental difficulties in evaluating the value of B directly from equation (15) this quantity was considered as a parameter of the model.

The model discussed can be applied to different situations of nucleate boiling of multicomponent liquid mixtures if appropriate mass transfer coefficients for the vanishing mass fluxes are known. The main problem in applying equation (6), which takes into account the mass resistance in the vapour phase, is an unknown concentration in the bulk of the vapour. This concentration, in the case of pool boiling, corresponds to the average concentration in the vapour bubble and was calculated using the following simplified matrix formula:

$$\mathbf{y} = \left[\mathbf{E} + (\mathbf{K}-\mathbf{E})\exp(-\boldsymbol{\Phi})\right]\mathbf{x} \qquad (17)$$

where the rate factor matrix $\boldsymbol{\Phi}$ is defined as

$$\boldsymbol{\Phi} = \boldsymbol{\Phi}_\mathrm{G} + \mathbf{K}\boldsymbol{\Phi}_\mathrm{L} \qquad (18)$$

The average concentration in the spherical vapour bubble can also be estimated from the simplified mass transfer model assuming one-dimensional convection to the bubble interface. In this analysis it is assumed that the bubble grows homogeneously in a superheated liquid until it reaches the departure diameter ($d = 2r$).

4. COMPARISON

The numerical calculations were done assuming that the diffusional resistance appears in either, or alternatively, both of the phases (liquid and vapour). The liquid phase mass transfer coefficient was evaluated from the Frössling equation [13] with w_L equal to 0.01 $\mathrm{m\cdot s^{-1}}$ for all the experiments. For the mass transfer in the vapour phase the Pieters correlation [14] was applied with w_G evaluated as the ratio of the total mass flux to the molar vapour concentration. The growth rate thus determined coincided with the experimental results of Thome and Davey [15]. The bubble departure diameter can be calculated from different correlations given in literature [5, 16–19]. In this work for calculations of mass transfer coefficient the bubble diameters were determined from the formula of Fritz and Ende cited by [5], which is sufficiently accurate for these purposes. The value of B, equation (15), was estimated in our experiments for the system methanol–isopropanol–water using the image processing software package GRCH developed for the frame grabber graphic card IP-8 (MATROX), over the range 1–5. For computational purposes this value was determined from a simple formula as a function of the bubble departure diameter for given mixture (d) and for water ($d_{\mathrm{H_2O}}$), calculated as follows:

$$B = 5\frac{d}{d_{\mathrm{H_2O}}} \qquad (19)$$

In this way the value of B was treated as a parameter of the model presented. When the calculations were done assuming that the diffusional resistance appears only in the liquid phase, better agreement with the experiments was obtained for B calculated from equation (19) than when it was taken as equal to one (*figures 2* and *3*).

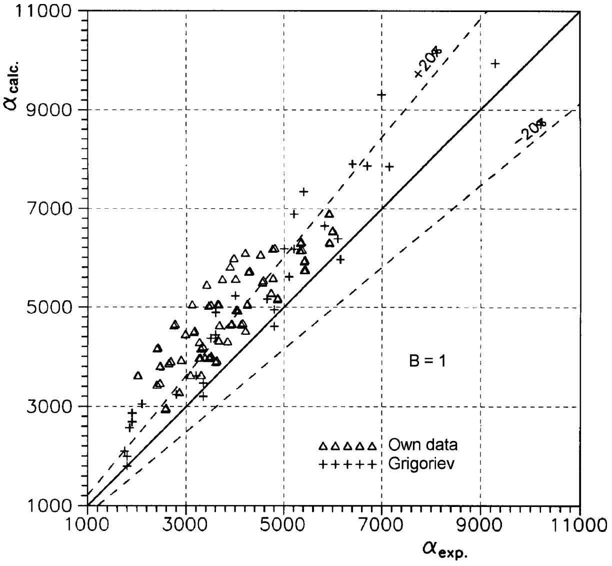

Figure 2. The results of numerical calculations with the diffusional resistance only in the liquid phase ($B = 1$).

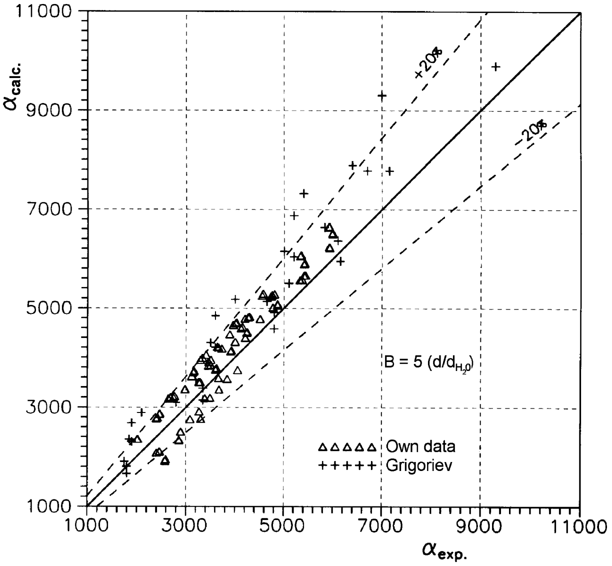

Figure 3. The results of numerical calculations with the diffusional resistance only in liquid phase ($B = 5d/d_{H_2O}$).

The results of calculations performed taking into account the effect of the diffusional resistance in both phases are presented in *figure 4* with the vapour composition **y** estimated from equation (17). In this case slightly better accuracy was achieved than that for the case when the diffusional resistance in the liquid phase only was taken into account (*figure 3*).

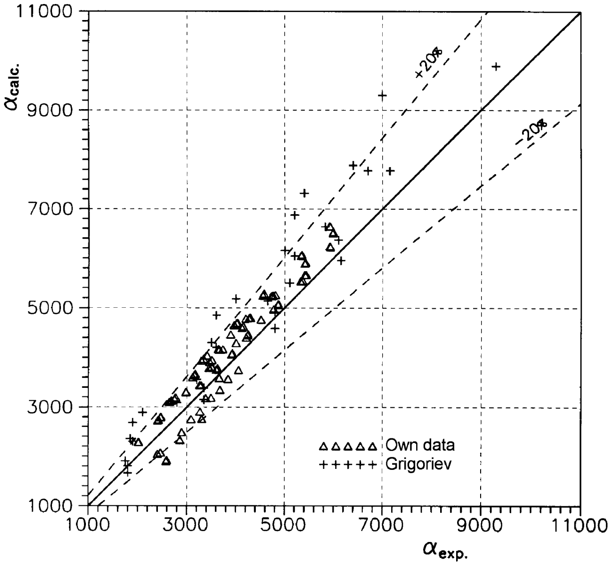

Figure 4. The results of numerical calculations with the diffusional resistance in both phases (**y** calculated from equation (17)).

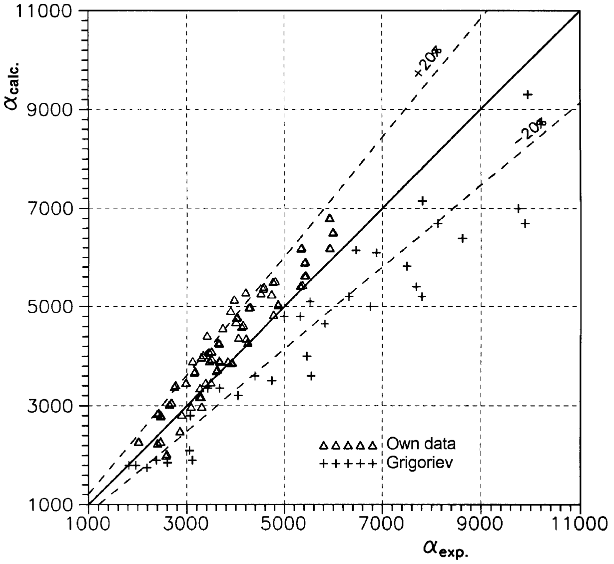

Figure 5. The results of numerical calculations with the interfacial temperature T_I assumed to be equal to the dew point temperature T_d.

When the ratio α/α_{id} is calculated directly from the basic equation (1) assuming that the liquid–vapour interfacial temperature is equal to the dew point of the vapour with the same composition as the liquid mixture, the reasonable results were obtained (*figure 5*).

5. CONCLUSIONS

- A mathematical model is presented based on multicomponent mass transfer theory. This model enables the effect of mass transport on heat transfer coefficients during the pool boiling of a mixture to be predicted with good accuracy when the *B* value (equation (19)) is treated as a parameter.
- The results of our own experimental study (*figure 1*) show that the minimum of $\alpha_{\mathrm{exp}}/\alpha_{\mathrm{id}}$ in the ternary system methanol–isopropanol–water is lower than that for the corresponding binary mixtures. A similar conclusion was reached by [1] for the system acetone–methanol–water.
- When the calculations are done with the assumption that the diffusional resistance appears in both phases (*figure 4*), the results are only slightly better than those obtained assuming that the diffusional resistance occurs only in the liquid phase (*figure 3*). This may lead to the interesting conclusion that under the pool boiling conditions the mass transfer resistance in the vapour phase can be neglected.

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