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NUCLEATE BOILING IN BINARY MIXTURES

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Abstract—It is well established that many parameters associated with nucleate boiling of a mixture differ significantly from those for a pure fluid of identical physical properties. Some authors attribute this difference to changes in bubble growth rates due, ultimately, to a resistance to the interdiffusion of the species. Others suggest that the change is due to differences in the superheat required to initiate bubble growth due, ultimately, to changes in the parameters governing the saturation pressure–temperature relationship.

The latter theory is closely examined here and found to be untenable. It is, however, shown that in aqueous systems there may be an increase in the superheat required for the onset of nucleate boiling due to the effects of the change in wetting characteristics for organic solvents at low concentrations. Experimental data abstracted from the literature show that the diffusion resistance which is found once boiling has commenced still plays a significant role in the reduction in heat transfer in aqueous systems and it is presumed to be the controlling factor in non-aqueous systems.

NOMENCLATURE

$\bar{G}$,	partial molar Gibbs free energy [J kmol^{-1}];
$\bar{h}_{LV}$,	molar latent heat of evaporation [J kmol^{-1}];
P,	pressure [N m^{-2}];
q,	heat flux [W m^{-2}];
R,	spherical bubble radius [m];
R_c,	cavity radius [m];
$\bar{S}$,	molar entropy [J kmol^{-1}];
T,	temperature [°C, K];
$\bar{V}$,	molar volume [m^3 kmol^{-1}];
x_i,	interface mole fraction of light component in liquid;
x_0,	bulk mole fraction of light component in liquid;
y^*,	equilibrium mole fraction of light component in vapour;
θ,	contact angle [rad];
σ,	surface tension [N m^{-1}].

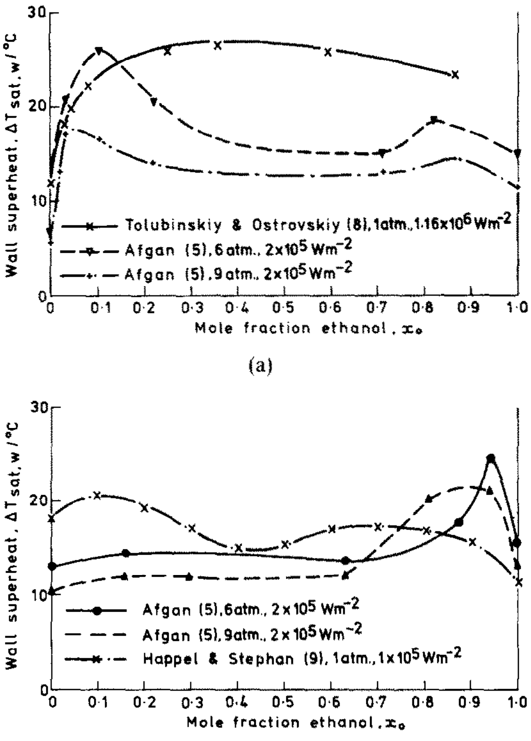
Subscripts

L,	liquid;
sat,	saturation;
V,	vapour;
W,	wall.

INTRODUCTION

THIS paper presents a study of the major factors influencing boiling heat transfer in binary mixtures. The conclusions are supported by data presented elsewhere by the present author [1] and by others.

It is well known [2–4] that the presence of an essentially incondensable gas in an otherwise pure fluid can cause a reduction in the superheat required (relative to the saturation condition of the pure fluid) for equilibrium of a bubble embryo of a given size. This superheat can indeed be negative. In this case the significant factor is the partial pressure exerted by the gas in the bubble. Once a bubble commences to grow the process is not influenced by the presence of the gas.



(a)

(b)

FIG. 1. Nucleate boiling data for mixtures: (a) Ethanol/water mixtures; (b) Ethanol/benzene mixtures.

This paper is, however, more concerned with binary mixtures wherein both phases contain both components in significant proportions. The onset of nucleate boiling is now a considerably more complex problem. It is by now well established [5–7] that, for nucleate pool boiling in a binary fluid mixture the heat transfer coefficient and bubble departure diameter are lower than in a pure fluid of identical physical properties while the critical heat flux is greater.

Figure 1 shows data for boiling of ethanol/water and ethanol/benzene mixtures. (The lines for ethanol/water in the paper of Afgan appear to have been incorrectly labelled and have been corrected here.) The data of Afgan [5] are for boiling on the outside of a horizontal cylindrical tube (5 mm dia) immersed in a static pool of liquid. Heating was achieved by passing an electrical current through the walls of the tube. The fluid was at its saturation temperature at the operating pressures of 6 and 9 atm. Tolubinskiy and Ostrovskiy [8] performed experiments on saturated boiling in a vertical stainless-steel tube of diameter 4.5 mm. They too used direct heating. Happel and Stephan [9] used a horizontal nickel tubular test-section immersed in a pool of fluid. Heating was by a combination of direct electrical heating and a fluid passing along the inside of the tube.

Although the graphs show differences in trends at intermediate concentrations it is clear that additions of small amounts of solutes to pure solvents result in significant increases in the wall superheats for given heat fluxes.

Many authors hold this reduction in heat-transfer coefficient to be due to a local depletion in the low boiling component at the liquid vapour interface once boiling has commenced. This causes the local saturation temperature to be greater than in the bulk fluid. The superheat $[T_w - T_{sat}(x_i)]$ which is then available to conduct heat towards the interface and thence into evaporation is thus less than it would be for a pure fluid $[T_w - T_{sat}(x_0)]$. The bubble growth rates are consequently reduced and so are the heat-transfer coefficients.

In this work x_0 is taken to be the mole fraction in the bulk liquid phase of the component which, in the pure state, has the lower boiling point; y^* is the vapour mole fraction in equilibrium with a liquid of concentration x_0. In most binary mixtures $y^* - x_0$ (which can be considered as the driving force for reducing bubble growth rates) is positive but for components which can form an azeotrope (constant boiling mixture) this quantity can be positive or negative. The theories linking the change in heat-transfer coefficient to bubble growth rate changes predict that, whatever is the sign of $y^* - x_0$, a reduction in bubble growth rate will always occur. This is experimentally confirmed in Fig. 1. Both mixtures concerned form azeotropes: for ethanol/benzene at 1 atm—$0.20 < (y^* - x_0) < 0.19$; and for ethanol/water at 1 atm—$0.05 < (y^* - x_0) < 0.35$ (see Fig. 2 for phase equilibrium diagram and for graphs of surface tension at saturation against liquid composition). These data were calculated using methods described by Shock [1]. Van Stralen [7] has noted that the maximum reduction in bubble growth rate and departure diameter and the maximum increase in critical heat flux occur at the same concentration, which, in turn, corresponds to a maximum in $y^* - x_0$. This concentration is often very low for aqueous systems, and depends on the relative volatility. Van Stralen [7] and Valent and Afgan [10] have measured bubble growth rates and confirmed that the decrease can be correlated with the difference $y^* - x_0$.

Some authors [5, 8, 11] hold the view that the cause of the observed changes in boiling characteristics in mixtures is an increase in the superheat required to maintain equilibrium of spherical bubble nuclei. This, they say, causes a decrease in the active site density and consequently in the heat flux for a given superheat.

In the following sections the equilibrium superheats for bubbles in two mixtures are calculated and compared with the qualitative predictions of these previous authors.

BUBBLE NUCLEATION AND SUPERHEAT

For a single-sided spherical bubble of radius R the pressure inside is greater than that outside by an amount ΔP given by

$$\Delta P = P_V - P_L = \frac{2\sigma}{R}. \tag{1}$$

The surface tension depends on the nature of the fluid and on its temperature.

In an equilibrium system with a uniform temperature the liquid will be superheated with respect to the saturation temperature T_{sat} at P_L. The superheat for a given radius can be found by solution of the equation

$$\int_{T_{sat}}^{T} \frac{dP_{sat}}{dT}\, dT = \frac{2\sigma}{R} \tag{2}$$

which can be obtained from equation (1). For low superheat equation (2) becomes

$$\Delta T_{sat} = 2\sigma/R \frac{dP_{sat}}{dT}. \tag{3}$$

For an ideal pure fluid it can easily be shown [12]

$$\frac{dP_{sat}}{dT} = \frac{\bar{S}_V - \bar{S}_L}{\bar{V}_V - \bar{V}_L} \tag{4}$$

which can be extended to give the Clausius–Clapeyron equation

$$\frac{dP_{sat}}{dT} = \frac{\bar{h}_{LV}}{T(\bar{V}_V - \bar{V}_L)}. \tag{5}$$

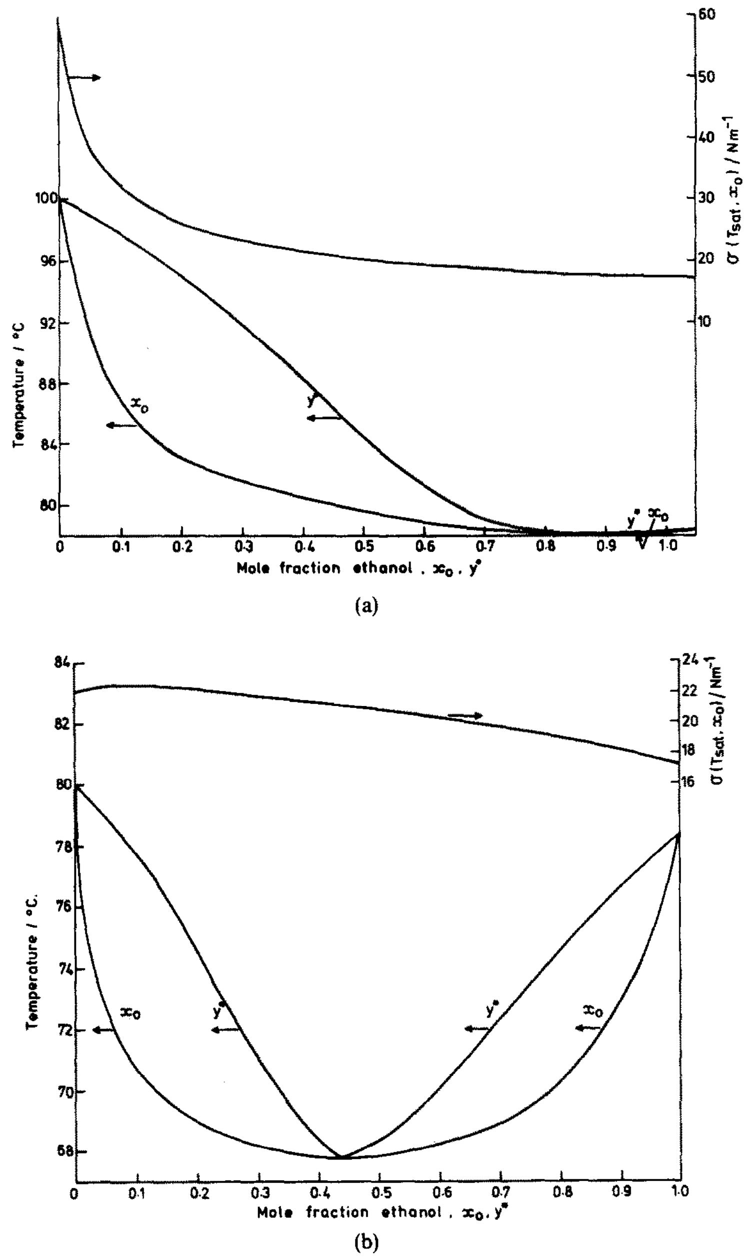
It can be seen from equation (3) that the value of dP_{sat}/dT may play a large part in determining the superheat requirement for bubble equilibrium.

Stephan and Korner [6] have shown that the equivalent to equation (4) for an ideal binary mixture at constant composition is

$$\frac{dP_{sat}}{dT} = \frac{\bar{S}_V - \bar{S}_L}{\bar{V}_V - \bar{V}_L} + \left(\frac{y^* - x_0}{\bar{V}_V - \bar{V}_L}\right)\left(\frac{\partial^2 \bar{G}}{\partial x^2}\right)_{T,P} \frac{\partial x}{\partial T_{sat}}. \tag{6}$$

The derivation of this and related equations is also discussed by Malesinsky [13].

Certain important conclusions arise from an examination of the extra group of terms in equation (6). Applying Konovalov's rule (the vapour is richer than the liquid with which it is in equilibrium in that component by addition of which to the system the vapour pressure is raised) we can deduce that $y^* - x_0$ and $\partial x/dT_{sat}$ are always of opposite sign. Furthermore $\bar{V}_V - \bar{V}_L$ is always positive and the basic rules of thermo-



(a)

(b)

FIG. 2. Phase equilibrium and surface tension data for mixtures: (a) Ethanol/water mixtures; (b) Ethanol/benzene mixtures.

dynamic equilibrium tell us that $\partial^2\bar{G}/\partial x^2$ is also always positive. Hence examination of the RHS of equation (6) shows that the group

$$\left(\frac{y^*-x_0}{\bar{V}_V-\bar{V}_L}\right)\left(\frac{\partial^2\bar{G}}{\partial x^2}\right)_{T,P}\frac{\partial x}{\partial T_{\text{sat}}}$$

is *always* negative. Previously, as shown by Shock [1] various authors have misinterpreted the sign of this group in certain concentration ranges for mixtures which form azeotropes. Note that this group tends to zero for the pure components and for azeotropic mixtures. Since, for all other cases, the group is always negative equation (6) shows that, for an ideal solution, $\mathrm{d}P_{\text{sat}}/\mathrm{d}T$ is always less than for an ideal pure substance of the same entropy and volume changes on evaporation (this ideal pure substance is henceforth known as the equivalent pure fluid, EPF). Grigor'ev [11] and others examined equation (3) in the light of this reduction and held that, since $\mathrm{d}P_{\text{sat}}/\mathrm{d}T$ is less than for the EPF, ΔT_{sat} is increased and that the consequent reduction in bubble population explains the decreases of heat-transfer illustrated in Fig. 1. It should be noted that this type of theory also predicts a reduction in coefficient whatever is the sign of y^*-x_0.

The authors who have propounded this theory did not consider the effects of changes of surface tension or of effective nucleus radius R due to changes in mixture composition (especially for aqueous solutions).

These effects, as well as those of dP_{sat}/dT, are examined here.

For a fluid/solid contact angle of less than $\pi/2$ (typical of most combinations) a bubble growing from within an idealised conical cavity passes through a minimum radius when it forms a hemisphere of radius R_c at the cavity mouth. If the contact angle is greater than $\pi/2$ the minimum radius will be that of a bubble at the mouth just before the three-phase interface begins to spread along the surface away from the cavity without the bubble reaching the hemispherical state.

The superheat requirement for a nucleus of the minimum radius is a maximum in the superheat-radius locus and it is this value which will usually determine whether or not a bubble can grow in a given cavity with a given superheat. It is at this stage assumed that a complete range of potentially active nucleation sites is available on the heating surface; this assumption is critically examined in a following section of this work.

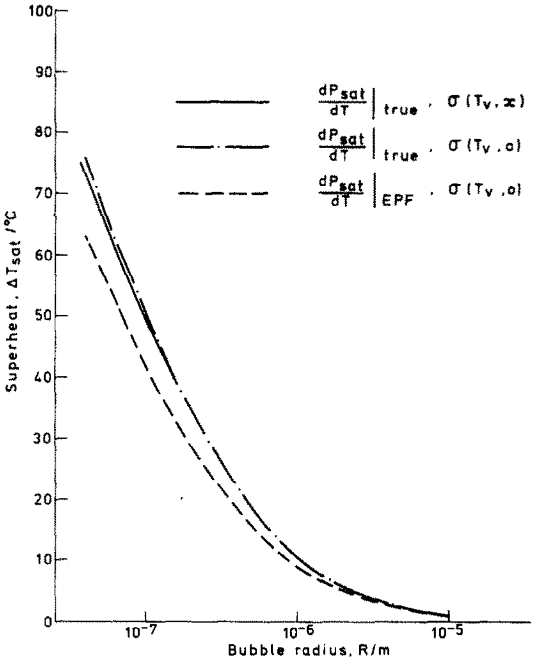


FIG. 3. Plot of superheat against radius for spherical vapour bubbles in ethanol/benzene solutions, $x_0 = 0.05$.

Figures 3 and 4 show theoretical superheats for the onset of nucleate boiling in ethanol/benzene and ethanol/water mixtures at 1 atm, in both cases $x_0 = 0.05$. The superheats are shown plotted against cavity sizes R_c. (The critical nuclei being hemispheres of that radius.) Calculation was carried out using equation (2) with $R = R_c$. See [1] for details of the iterative procedure. The figures show three values of superheat, i.e.

(a) The true value for the mixture.

(b) The value using the true value of dP_{sat}/dT but the surface tension of the pure solvent, $\sigma = \sigma(T_V, 0)$.

(c) The value using dP_{sat}/dT equivalent to the EPF and using the surface tension of the pure solvent, $\sigma = \sigma(T_V, 0)$.

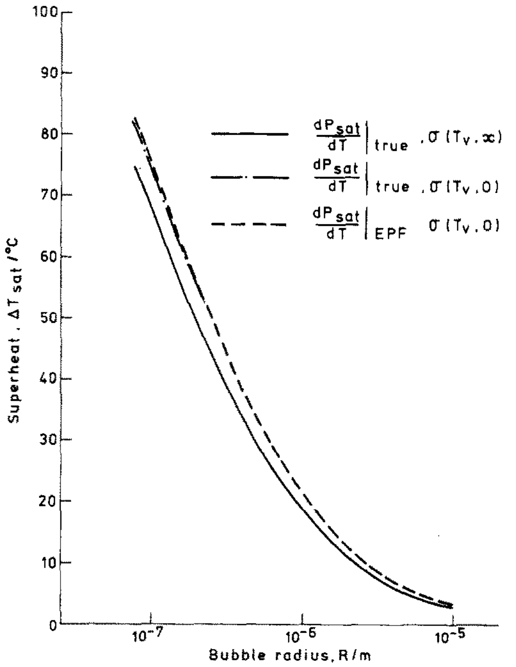


FIG. 4. Plot of superheat against radius for spherical vapour bubbles in ethanol/water solutions, $x_0 = 0.05$.

Previous workers in examining only the effect of dP_{sat}/dT have effectively compared values (b) and (c). The figures show that, in the case of ethanol/benzene mixtures, the influence of dP_{sat}/dT alone is indeed, as predicted earlier, to cause the superheat for the mixture to be higher than for the EPF. A similar, though much smaller, effect is found with ethanol/water mixtures. Extending the argument to the third curve, to examine the effect of surface tension changes, we can see that their effect is small in the case of ethanol/benzene mixtures, where the surface tension is only a weak function of concentration. However, for aqueous ethanol mixtures, where the surface tension decreases markedly at low x_0 for increasing x_0, the effect of surface tension changes completely overrides those of dP_{sat}/dT and appears to indicate a marked drop in the superheat.

Further important results can be gathered from Fig. 5 which examines the effect of composition on the superheats using the true values of dP_{sat}/dT but, following Grigor'ev and others, neglecting surface tension changes. The graphs show that, for a given cavity size, additions of ethanol to pure benzene or water appear to *decrease* the superheat requirement. This contradicts the conclusions drawn by previous workers of the effects of dP_{sat}/dT as deduced from equation (6) and used as an explanation of the results shown in Fig. 1.

To resolve this paradox values of dP_{sat}/dT were calculated over the entire concentration range for both mixtures and these are shown in Figs. 6 and 7. Values were calculated in two ways. The first is the true value for the mixture concerned, i.e. that which would be predicted by equation (6). Because of the difficulties in calculating Gibbs free energies the calculations were actually performed using bubble point methods described by Shock [1]. $\mathrm{d}P_{sat}/\mathrm{d}T$ was given by

$$\frac{\mathrm{d}P_{sat}}{\mathrm{d}T} = \lim_{\delta T \to 0} \frac{P_{sat}(T+\delta T) - P_{sat}(T-\delta T)}{2\delta T} \tag{7}$$

δT was taken in successively smaller steps until the results given by equation (7) converged. This occurred at $\delta T = 0.01$°C.

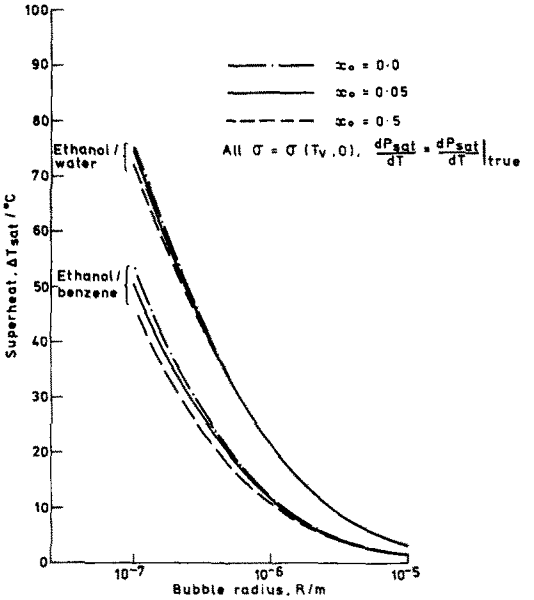


FIG. 5. Plot of superheat against radius for spherical vapour bubbles. Effect of composition.

The second value of $\mathrm{d}P_{sat}/\mathrm{d}T$ shown in Figs. 6 and 7 is that of the EPF. These were calculated from equation (5) neglecting $\bar{V}_L$ in comparison with $\bar{V}_V$. The latent heat of evaporation was taken, following Stephan and Korner [6], to be the integral value (the amount of heat required to evaporate completely a unit quantity of material). Values for ethanol/water were obtained from the data given by Shock [1] and for ethanol/benzene from the work of Tyrer [14] (he calls the integral latent heat the constant composition quantity).

Examining Figs. 6 and 7 we can see that the two calculations of $\mathrm{d}P_{sat}/\mathrm{d}T$ for the pure substances have produced results which differ by no more than 1.3%. Thus the ideality assumption in equations (5) and (6) appears reasonable and there is no reason to suppose it to be invalid for the EPF's of the mixtures.

It can be seen that for ethanol/benzene mixtures the true value of $\mathrm{d}P_{sat}/\mathrm{d}T$ is indeed less, by as much as 16%, than the value for EPF. For ethanol/water mixtures there appears in contrast to be a slight increase; this, however, is but 1% and is of the same order of magnitude as the error due to the (slight) non-ideality. Thus, essentially, $\mathrm{d}P_{sat}/\mathrm{d}T$ is the same as for the EPF—a point already shown up by the the data in Fig. 4.

A further point, and one of the main conclusions of this work is that the addition of ethanol to benzene and to water and of water to ethanol *increases* $\mathrm{d}P_{sat}/\mathrm{d}T$; the increase is indeed somewhat less than it would be for the EPF but it nonetheless occurs. Thus, we might expect, ignoring changes in σ and in effective R_c, that addition of ethanol to the pure solvents would cause a reduction of superheat for onset of nucleate boiling, ONB. This has indeed been illustrated in Fig. 5. Finally, we note that only in the case of addition of benzene to ethanol does a reduction in $\mathrm{d}P_{sat}/\mathrm{d}T$ occur.

Certain conclusions can be drawn from the results so far presented.

(a) The reduction of $\mathrm{d}P_{sat}/\mathrm{d}T$ compared with the value for the EPF has been confirmed.

(b) The value of $\mathrm{d}P_{sat}/\mathrm{d}T$ for solutions of ethanol in benzene and water and of water in ethanol is *higher* than for the pure solvents. Theories linking the changes

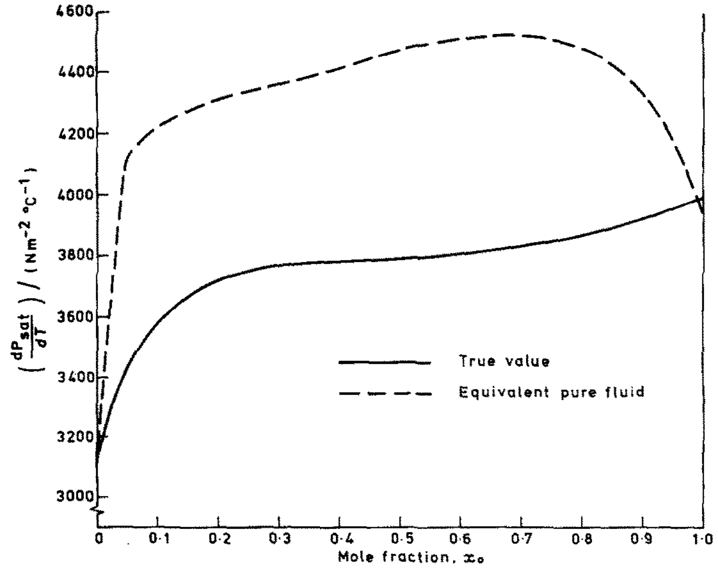


FIG. 6. Values of $\mathrm{d}P_{sat}/\mathrm{d}T$ for ethanol/benzene mixtures.

in heat transfer coefficients with changes in bubble populations through decreases in dP_{sat}/dT cannot thus be generally tenable even though the changes appear to be in the correct direction for addition of benzene to ethanol.

(c) The surface tensions of aqueous ethanol solutions are very sensitive to concentration. The effect on the equilibrium superheat requirement outweighs any due to changes in dP_{sat}/dT and would appear to predict a *decrease* on addition of ethanol to water.

EXPERIMENTAL EVIDENCE

The theory presented so far has considered the equilibrium of spherical bubbles in infinite volumes of uniformly superheated liquid or of the equivalent hemispherical nuclei at the tips of ideal conical cavities. We now consider the growth of bubbles on real metal surface where the properties of the third (solid) phase may add a further, complicating, factor.

Table 1. Data for incipient bubble nucleation

x_0	T_w (°C)	$\Delta T_{sat,w}$ (°C)	$10^{-6} \times R_c$ (m)	$P \times 10^{-5}$ (N m^{-2})
0	138.2	9.9	1.05	2.61
0.058	143.5	26.6	0.23	2.59
0.197	145.0	36.7	0.095	2.47

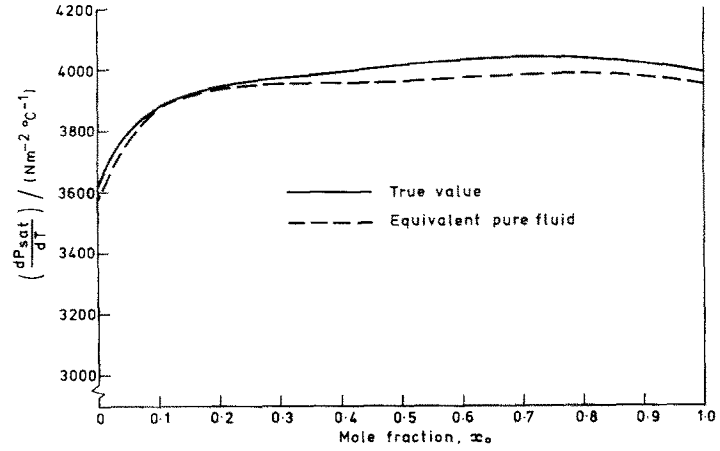


FIG. 7. Values of dP_{sat}/dT for ethanol/water mixtures.

Recent experiments by Shock [1] on convective boiling of ethanol/water mixtures in heated channels have shown that as x_0 increases, there is a large increase in superheat for ONB with a consequent reduction in active site density. This finding should be contrasted with the result shown in Fig. 5 that the combined effects of changes in dP_{sat}/dT and in σ should cause a large reduction in the ONB superheat.

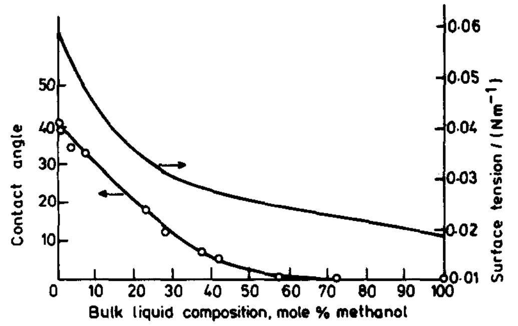
Experiments were performed in a 22 mm I.D. circular tube of length 3.05 m, heated by an electric current passing through its walls. The fluid flowed vertically upward through the tube. The surface was of nickel plating on a copper tube. The operating pressure was approximately 2.5 atm. Wall temperatures were recorded at various axial distances and boiling inception was inferred from sudden changes in the slope of the temperature profile. From a large number of data only those giving clear evidence have been included. Table 1 shows some of the results obtained.

Values of R_c have been evaluated assuming the critical nucleus to be a hemisphere at the mouth of a conical cavity. The sizes were located graphically by locating the intersection of the equilibrium superheat-radius curve with the actual superheat profile in the liquid layer near the wall assuming laminar conduction only. The method assumes the entire equilibrium bubble to be, effectively, at the tip temperature; the gradients in this case are, however, small. For further details of the method see [1].

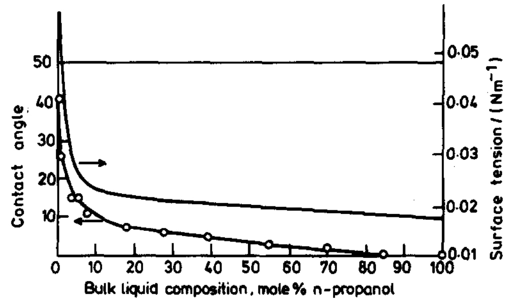
The prediction method for ONB of Davis and Anderson [15] (based on the tangency of the equilibrium superheat-radius curve and the superheat profile), which assumes a complete range of potentially active nuclei, predicts that nucleate boiling in pure water should commence at a wall superheat of 0.9°C, with an effective nucleus radius of 12.2×10^{-6} m. Cavities of such size are likely to be completely filled with liquid and hence not to be available as potential nuclei. A superheat of 9.9°C with a radius of 1.05×10^{-6} m (see Table 1) is typical of values found with water, this being the largest cavity which is not completely filled.

Table 1 shows that addition of ethanol to water even to x_0 as low as 0.058 causes ONB superheats for the same surface to be markedly increased. The earlier predictions that the superheats should be reduced arose out of consideration of σ and dP_{sat}/dT in equation (3). The explanation of these results is linked to the apparently overriding affect of the change in wetting characteristics on the availability of potential nucleation sites and to a possible change in the effective radius.

It is suggested that the large increase in superheat ONB and reduction in related cavity size is due to the well-wetting ethanol solutions causing a greater proportion of the cracks in the tube wall to fill completely with liquid. Ponter *et al.* [16] have shown that the



Equilibrium contact angles for methanol-water-graphite system.



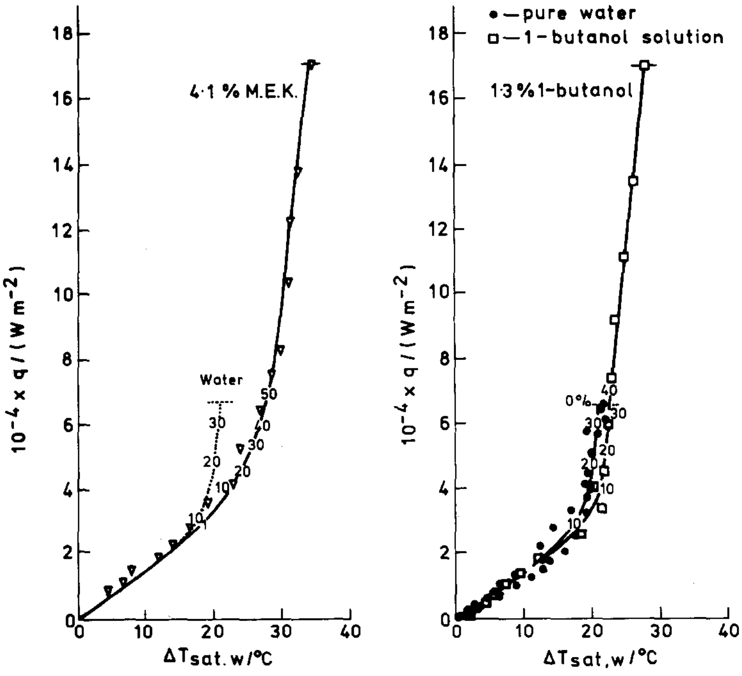
Equilibrium contact angles for n-propanol-water-graphite system.

FIG. 8. Equilibrium contact angles. Data of Ponter *et al.* [16].

contact angles of alcohol/water solutions decrease as x_0 increases, especially at low x_0 see Fig. 8. Note that the shape of the θ–x_0 locus is similar to that of the σ–x_0 locus. Bankoff [17] has shown that when the contact angle is less than the conical angle the cavity will be "snuffed out". Thus where a cavity was trapping gas for an advancing water front it may no longer do so for the aqueous ethanol solutions and former potentially active cavities are lost. The largest nucleus present is thus reduced and the corresponding ONB superheat is increased.

A further possible mechanism for increasing the ONB superheat is suggested by the work of Lorenz *et al.* [18]. The results presented so far have considered the critical nucleus to be a hemisphere at the cavity mouth since this represents a local maximum in the superheat-radius locus. At lower bubble radii (for nuclei lower in the cavity) there is a local minimum and nuclei of smaller radius still (smaller indeed than the cavity radius) can require a superheat greater than those at the maximum. Lorenz *et al.* have shown that, for a given cavity, a reduction in contact angle can so lower the effective radius that this requirement begins to control. They carried out pool boiling experiments with water and organic fluid on a polished copper surface and found an effective cavity radius for water about twice that for the organics; the contact angle for all the organics was about 7° compared with 35° for water. It is thus suggested that, in the experiments described here, an advancing front of the low contact angle ethanol solution which does not succeed in completely filling the cavity may nonetheless form a nucleus of such small radius as to require a considerably greater superheat than that required by the hemisphere at the cavity mouth.

Further evidence on the onset of nucleate boiling in aqueous solutions can be obtained from the work of Van Stralen [19]. He gives boiling curves for pure water and for aqueous solutions of methylethyl ketone and 1-butanol boiling on thin wires (diameter = 2×10^{-4} m). He includes data for numbers of active nuclei observed. The following table is abstracted from his results, examples of which are shown in Fig. 9. The



methylethyl ketone 4·1 wt.%

1-butanol 1·3 wt.%

FIG. 9. Nucleate pool boiling data of Van Stralen [19] for aqueous solutions boiling on thin wires at 1 atm.

operating pressure was 1 atm. Note the large heat flux contributions from a combination of forced and natural convection especially at low bubble populations.

Table 2. Nucleate pool boiling data of Van Stralen

Number of active sites	Water		4.1% wt MEK		1.3% wt 1-butanol	
	$\Delta T_{sat,w}$	$q \times 10^{-5}$	$\Delta T_{sat,w}$	$q \times 10^{-5}$	$\Delta T_{sat,w}$	$q \times 10^{-5}$
1	10.5	1.67	18.0	2.93	18.0	2.59
10	17	2.93	23.0	3.97	21.5	3.98
20	20	4.81	24.0	4.68	22.0	5.27
30	21	6.06	26.0	5.44	22.5	6.27

These data confirm that the superheat required to cause activation of the first few nucleation sites is much greater in aqueous organic solutions than in pure water. The difference diminishes as a greater proportion of the potentially active nucleation sites become activated.

The contribution to the total heat transfer from combined forced and natural convection in the space between the bubbles was found by extrapolating the lower region of the "boiling curve". The contribution due to bubble growth was then calculated by subtraction. The corresponding boiling-only heat-transfer coefficients are listed in the following table.

Table 3. Nucleate boiling heat-transfer coefficients

Number of active sites	Water	4.1% wt MEK	1.3% wt 1-butanol
10	2470	2348	3906
20	9400	4333	9318
30	14095	5961	13155

In general we see that, for a given number of active nucleation sites, the coefficient decreases on addition of small amounts of organic solvents to water. Table 2 shows that not only are the coefficients reduced but the corresponding superheats are increased. The apparently anomalous point for 1.3% 1-butanol with ten active sites may be due to the scatter in the data. Since we can compare purely nucleate boiling coefficients for constant numbers of active nucleation sites it is now possible to confirm that the previously measured reduction in bubble growth rates [7, 10] will play a significant part in the reduction in heat-transfer coefficient. This reduction in coefficient due to the diffusion resistance acts in addition to the role played by the reduction in nucleation site density for given superheat.

It has been shown that, at least for dilute solutions of ethanol in benzene, the bubble population may increase. Hence we can confirm the overriding effect in producing the reduction in heat-transfer coefficient in that mixture (illustrated in Fig. 1) to be diffusion resistance reducing bubble growth.

CONCLUSIONS

Theories which account for the observed reduction of heat-transfer coefficients in mixtures by a decrease in dP_{sat}/dT below the value for the EPF cannot account for the changes in aqueous solutions nor for all of those in binary organic mixtures.

The effect of surface tension changes in most organic/organic mixtures is small. The effect in aqueous solutions is to indicate, as x_0 increases at low x_0, a large decrease in the superheat required for equilibrium of a spherical bubble.

For boiling of aqueous solutions on heating surfaces the superheat for ONB is dominated by the low contact angles. These have the effect of "snuffing out" otherwise potentially active sites.

For aqueous solutions the observed reduction of heat-transfer coefficient is, however, at least partly due to the change in saturation temperature at the growing bubble interface due, ultimately to the diffusion resistance. This effect is predominant in non-aqueous solutions.

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EBULLITION NUCLEE DANS LES MELANGES BINAIRES

Résumé—On sait que les nombreux paramètres associés à l'ébullition nucléée d'un mélange différent sensiblement de ceux d'un fluide pur de propriétés physiques identiques. Quelques auteurs attribuent cette différence à des changements de vitesse de croissance de bulle, dûs principalement à une résistance à l'interdiffusion des espèces. D'autres suggèrent que le changement est dû aux différences de surchauffe nécessaire à l'initiation de la croissance de la bulle, à cause de la modification des paramètres gouvernant les relations entre température et pression. La dernière théorie est examinée de près ici et elle est insoutenable. On montre que dans les systèmes aqueux, il peut y avoir un accroissement de la surchauffe nécessaire à l'initiation de l'ébullition nucléée, à cause du changement des caractéristiques du mouillage des solvants organiques en faible concentration. Des données expérimentales antérieures montrent que la résistance à la diffusion qui a déjà été trouvée jouer un rôle sensible dans la réduction du transfert thermique dans les systèmes aqueux, est considérée ici comme le facteur déterminant dans les autres systèmes.

BLASENSIEDEN BINÄRER GEMISCHE

Zusammenfassung—Es ist bekannt, daß viele Parameter für das Blasensieden von Gemischen stark von denen für eine reine Flüssigkeit mit identischen Stoffwerten abweichen. Einige Autoren führen dies auf Änderungen der Blasenwachstumsrate zurück, hervorgerufen durch einen zusätzlichen Diffusionswiderstand. Andere Autoren geben als Begründung die Änderung der zur Bildung einer Blase notwendigen Übertemperatur an, was auf der Änderung des Zusammenhangs zwischen Sättigungstemperatur und Sättigungsdruck beruht. Die letztgenannte Theorie wird hier eingehend untersucht und als unhaltbar befunden. Es wird jedoch gezeigt, daß eine Zunahme der zur Blasenbildung erforderlichen Übertemperatur infolge einer Veränderung der Benetzungseigenschaften bei wäßrigen Lösungen organischer Stoffe und bei niedrigen Konzentrationen möglich ist. Versuchsdaten aus der Literatur zeigen, daß der Diffusionswiderstand bei ausgebildetem Blasensieden jedoch auch in wäßrigen Systemen eine bedeutende Rolle bei der Verminderung des Wärmeübergangs spielt; es wird vermutet, daß dies bei nicht-wäßrigen Systemen der vorherrschende Faktor ist.

ПУЗЫРЬКОВОЕ КИПЕНИЕ БИНАРНЫХ СМЕСЕЙ

Аннотация — Известно, что многие параметры процессов пузырькового кипения смесей значительно отличаются от параметров кипения чистых жидкостей с идентичными физическими свойствами. Некоторые из авторов объясняют это различие изменениями скоростей роста пузырьков из-за сопротивления, вызываемого взаимной диффузией компонентов смеси. По мнению других, оно обусловлено различной степенью перегрева жидкости, которая требуется для начала роста пузыря из-за изменения параметров, определяющих соотношение между давлением насыщения и температурой. Проведен подробный анализ последнего положения и показана его несостоятельность. Однако отмечено, что степень перегрева в водных системах, требуемая для начала пузырькового кипения, может возрастать из-за изменения смачивающих свойств органических растворителей при их небольшой концентрации. Опубликованные экспериментальные данные свидетельствуют о том, что возникающее в начале кипения диффузионное сопротивление все же оказывает существенное влияние на уменьшение теплоотдачи в водных системах. Предполагается, что в неводных системах диффузионное сопротивление является определяющим фактором.