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NUCLEATE BOILING IN BINARY MIXTURES

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Abstract—When a binary surface tension positive system boils, a maximum nucleate boiling heat flux is exhibited at a low concentration of the more volatile component. A number of theories have been propounded to account for this behaviour. In this investigation contact angles and surface tensions have been assessed for low concentrations of aqueous methanol and *n*-propanol under mass-transfer conditions simulating that encountered during nucleate boiling. The data confirm that small bubble production with accompanying high heat transfer is to be expected.

NOMENCLATURE

g, acceleration due to gravity (LT^{-2});
m, film thickness (L);
u, point film velocity (LT^{-1});
y, film depth where velocity $= u$ (L).

Greek symbols

θ_m, contact angle at total reflux;
μ, liquid viscosity ($ML^{-1}T^{-1}$);
ρ, liquid density (ML^{-3});
σ_m, surface tension at total reflux (MT^{-1});
Γ, peripheral liquid flow rate ($ML^{-1}T^{-1}$).

INTRODUCTION

A NUMBER of investigations have been carried out in the last few years to ascertain the types of liquid mixtures which exhibit high nucleate boiling heat fluxes. Explanations for the increase in nucleate boiling which results when a second component is added to a pure liquid are inconsistent. The various mechanisms postulated to account for this behaviour have been summarised recently by Shock [1] who also showed that the difference in the superheat required to initiate bubble growth was influenced by wetting changes at low organic concentrations for aqueous organic solvent mixtures. He deduced that the diffusion resistance encountered when boiling had commenced played a significant role for aqueous systems and furthermore was probably the controlling factor for non-aqueous systems. His conclusions were based upon the wetting behaviour of aqueous methanol and *n*-propanol mixtures exhibited under equilibrium conditions at the boiling point which had been reported by Ponter *et al.* [2, 3]. If the wetting properties of such systems under conditions of total reflux, that is where the vapour and liquid have the same composition and are not in equilibrium are considered instead, then different conclusions can be drawn which explain the difference in behaviour between the nucleate boiling of surface tension positive and negative mixtures as well as the peak flux exhibited at low compositions. The reason for considering the wetting under these new conditions is that the bubble frowth rate is so high that there will certainly be insufficient time for equilibrium to be established. The purpose of this paper is to re-examine Shock's analysis using total reflux wetting data.

DISCUSSION

Contact angles have been measured for aqueous methanol and *n*-propanol mixtures at the boiling point both under conditions of equilibrium and where the vapour and liquid have the same composition (total reflux) using the cells described by Ponter *et al.* [3]. In a true boiling situation the solid surface is at a higher temperature than that encountered under distillation conditions but the effect of temperature on contact angle is known to be small [4] usually of the order of < 0.06 degree/°C, the mass transfer having the overwhelming influence. The contact angles were measured on a smooth copper surface, the reproducibility of data being better than $\pm 1°$. The contact angle composition data for the two systems are presented in Figs. 1 and 2.

In Shock's analysis it was assumed that the contact angles and surface tensions employed were those measured at equilibrium. As previously stated this is unlikely to be the case since insufficient time will have accrued to establish such conditions in a bubble. An indirect method has recently been developed to estimate surface tensions of surface tension positive systems at total reflux by Ponter *et al.* [5] which essentially analyses the forces maintaining a dry patch formed when the liquid flow rate down a vertical surface is reduced below that necessary to maintain a discrete film. A schematic diagram is shown in Fig. 3.

The surface tension forces along YC balance the fluid force brought about by the loss in momentum in bringing the liquid to rest at point y.

So

$$\int_0^m \rho u^2 \, dy = \sigma_m (1 - \cos\theta_m) \qquad (1)$$

where σ_m is the surface tension when mass transfer is

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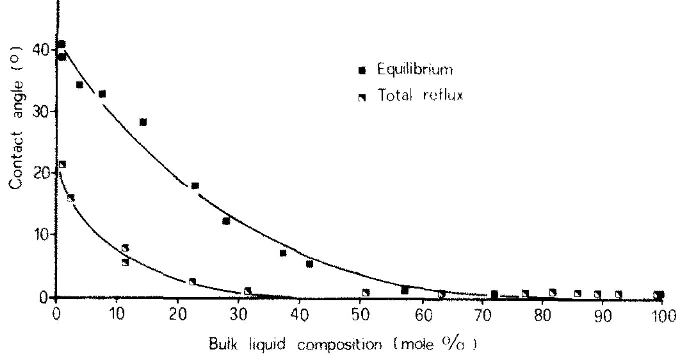

Fig. 1. Comparison of contact angle data at equilibrium and total reflux for methanol–water–copper system.

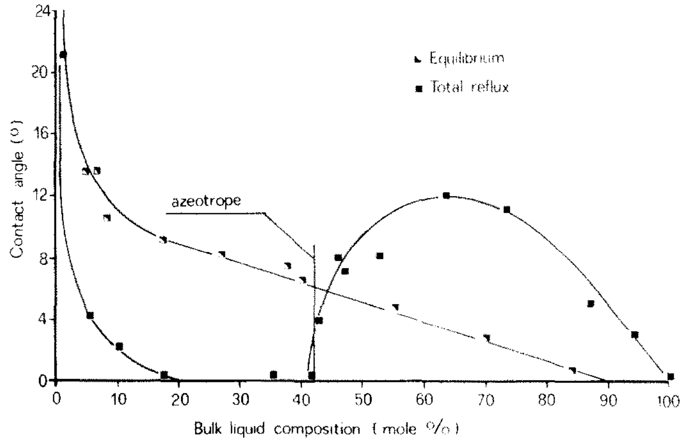

Fig. 2. Comparison of contact angle data at equilibrium and total reflux for *n*-propanol–water–copper system.

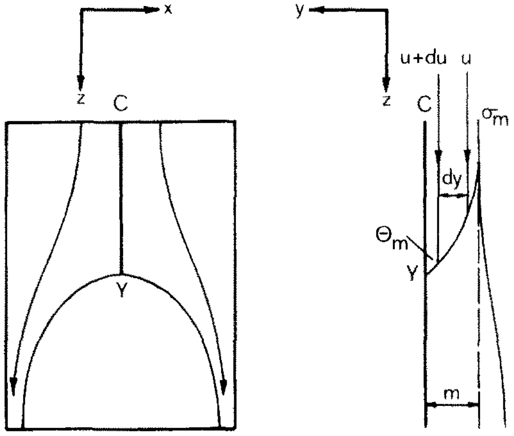

Fig. 3. Schematic diagram of dry patch.

occurring and θ_m is the corresponding contact angle through which fluid is flowing.

Now since the film rupture always occurs well within the laminar flow regime

$$u = \frac{\rho g}{2\mu}(m^2 - y^2) \tag{2}$$

so that substitution of equation (2) in (1) and integration yields

$$\frac{\Gamma}{\mu} = 1.12(1-\cos\theta_m)^{0.6}\left(\frac{\rho\sigma_m^3}{\mu^4 g}\right)^{0.2} \tag{3}$$

where Γ is the peripheral flow rate at which the dry patch just forms. Surface tension estimates for the two systems at total reflux are compared with the equilibrium values in Figs. 4 and 5.

It is readily seen that at low concentrations, the surface tensions exhibited under mass transfer conditions are considerably lower than for those determined at equilibrium. This explains the apparently anomalous behaviour of maximum boiling heat flux coinciding with maximum contact angle for a number of surface tension positive systems measured by Ponter *et al.* [6]. The high contact angle suggests the evolution of large bubbles with a subsequent low boiling heat flux. From the surface tension data now described however it is evident that the low tension values when combined with the high contact angles will still result in a low bubble adhesion giving small size bubble evolution and high nucleate boiling heat-transfer rates.

For surface tension negative systems no peak flux is observed and it is suggested that the interfacial turbulence is so high for these types of systems that equilibrium is quickly established and the mechanism now described will not be operative.

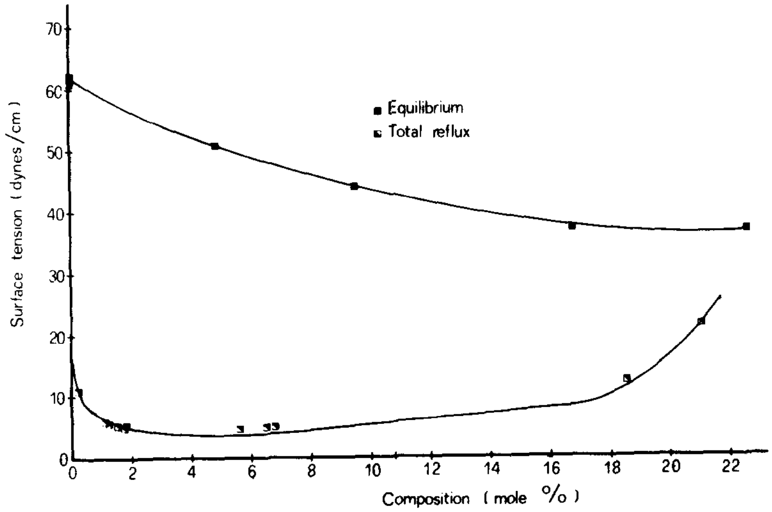

FIG. 4. Comparison of surface tension data at equilibrium and total reflux for methanol–water system.

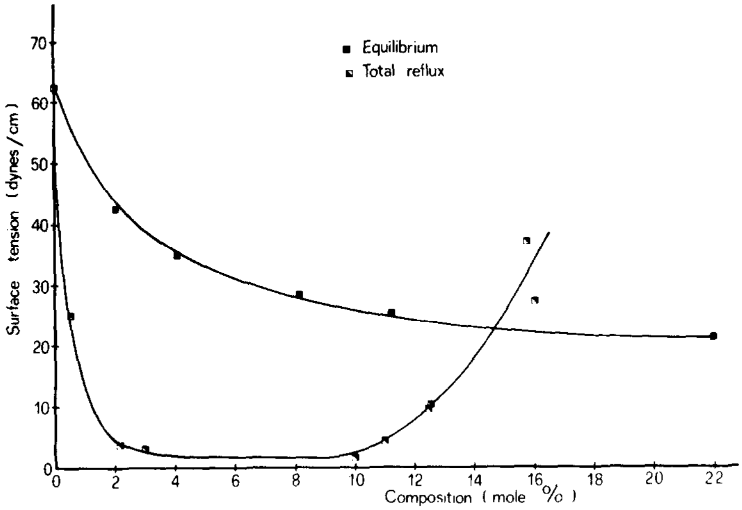

FIG. 5. Comparison or surface tension data at equilibrium and total reflux for *n*-propanol–water system.

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EBULLITION NUCLEEE DANS LES MELANGES BINAIRES

Résumé—Quand un système binaire à tension de surface positive bout, le flux thermique maximal d'ébullition nucléée apparait à une concentration faible du composant le plus volatil. Plusieurs théories ont été proposées pour expliquer cela. Dans cette étude, des angles de contact et des tensions de surface ont été évalués pour de faibles concentrations de méthanol et de *n*-propanol dans des conditions de transfert massique simulant celles de l'ébullition nucléée. Les résultats confirment qu'on peut espérer une petite production de bulle associée à un transfert thermique élevé.

BLASENSIEDEN IN BINÄREN GEMISCHEN

Zusammenfassung—Wenn ein binäres Gemisch mit positiver Oberflächenspannung siedet, weist es bei geringer Konzentration der leichter flüchtigen Komponente eine maximale Wärmestromdichte beim Blasensieden auf. Zahlreiche Theorien wurden vorgeschlagen, um dieses Verhalten zu erklären. In dieser Untersuchung wurden Kontaktwinkel und Oberflächenspannungen für wäßrige Methanol- und Propanolmischungen geringer Konzentration abgeschätzt. Die beim Blasensieden auftretende Stoffübertragung wurde simuliert. Die Ergebnisse bestätigen, daß geringe Blasenerzeugung bei gleichzeitiger hoher Wärmeübertragung erwartet werden muß.

ПУЗЫРЬКОВОЕ КИПЕНИЕ В БИНАРНЫХ СМЕСЯХ

Аннотация — При закипании бинарной смеси, имеющей положительное поверхностное натяжение, максимальный тепловой поток при пузырьковом кипении смеси наблюдается при малых концентрациях более летучего компонента. Предложен ряд теорий для объяснения этого явления. В данной работе определялось влияние контактных углов и поверхностного натяжения для водных растворов метанола и *n*-пропанола малой концентрации в условиях массопереноса, моделирующих условия пузырькового кипения. Полученные результаты свидетельствуют о том, что следует ожидать небольшого образования количества пузырьков при высоких значениях коэффициента теплообмена.