INTERFACIAL STABILITY IN BINARY LIQUID-LIQUID SYSTEMS

Thesis submitted for the Degree of
DOCTOR OF PHILOSOPHY
in the Faculty of Engineering of the
University of London

by

ELBA SUSANA PEREZ, M.Sc., D.I.C.

Department of Chemical Engineering and
Chemical Technology,
Imperial College of Science and Technology,
London S.W.7. July 1971

ABSTRACT

An attempt has been made to predict the onset of spontaneous Marangoni-type interfacial convection in binary partially miscible systems. The continuity and energy equations were solved simultaneously incorporating heat effects introduced by the heat of solution accompanying mass transfer. A linearized perturbation analysis was applied to the resulting temperature and concentration profiles. The stability criteria show that binary systems may be either stable or unstable in both directions of transfer or unstable in only one direction of transfer. They also suggest that stationary instability is promoted when the heat of solution and the rate of change of interfacial tension with temperature are of opposite signs and that instabilities of oscillatory character are most likely to occur for mass transfer out of the phase of higher viscosity. Good agreement was found with the experimental observations on six selected systems.

To my mother

ACKNOWLEDGEMENTS

I wish to express my deep gratitude to Dr. H. Sawistowski for his valuable advice, helpful suggestions and kind encouragement during the course of this work.

I would also like to acknowledge the British Council for the award of a grant to carry out this research, and the Universidad Nacional del Sur, Argentina, for a very generous leave of absence in addition to financial support during my studies at Imperial College.

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CHAPTER 1

INTRODUCTION

According to the simplest model of interface mass transfer, solute is transferred between two phases by processes of eddy diffusion, molecular diffusion and adsorption and desorption at the interface, all connected in series. The diffusional steps are normally rate controlling and the adsorption and desorption processes are generally fast enough to be neglected. However, the physical transfer across the interface is not the only way in which the interface can affect a mass transfer process. The interfacial tension, which is the result of almost a step change in the molecular fields of forces at the phase boundary, may be subjected to local fluctuations as a result of local variations in temperature or concentration. Such a fluctuation will affect the balance of forces and result in interfacial flow (Marangoni effect).

The Marangoni effect can affect a mass transfer process in two ways - by influencing either the area of contact of the phases or the mass transfer coefficients. The first effect predominates if the depth of penetration of interfacial movement is of the same order of magnitude as the actual depth of the liquid layer (thin film effects). The second effect is important if the depth of the liquid layer is significantly greater than the depth of penetration of interfacial movement. Under suitable conditions, the interface then acts as a source of interfacial convection, and appreciably higher mass transfer coefficients.are obtained (surface renewal effect).

An experimental study of the effect of interfacial convection on mass transfer coefficients requires the availability of reference correlations obtained under interfacially stable conditions. It was thought that such conditions could easily be attained by investigating the mass transfer characteristics of partially miscible binary systems. Such systems not only yield individual or "film" mass transfer coefficients, which are much easier to handle than overall coefficients obtainable from ternary systems but, in addition, they were expected to be free of interfacial convection. This belief was based on the assumptions that thermal effects in mass transfer between partially miscible binary systems are negligibly small and that equilibrium at the interface is always attained instantaneously. Consequently, according to the phase rule, the system should have no degrees of freedom at the interface which precludes the formation there of concentration gradients and thus interfacial tension gradients.

The assumed freedom of partially miscible binary systems from spontaneous interfacial convection of the Marangoni type was not confirmed experimentally. It indicates that the assumptions under which the phase rule was applied to interfacial conditions may not be valid. Thus, thermal effects due to heats of solution may not be negligible but introduce the desired degree of freedom and / or dynamic interfacial effects are present resulting from compression and dilatation of the surface layer or a finite rate of equilibrium of the interface. In the latter case the phase rule would no longer be applicable.

The purpose of the present work was an attempt of theoretical prediction of the appearance of spontaneous Marangoni-type interfacial convection in binary systems. It was assumed that interface equilibration was instantaneous. This was considered justified in view of the nature of the interface in partially miscible binary systems. The compression and dilation effect, although present in the basic formulation,was neglected in the final analysis for the same reason. It is therefore assumed that instabilities are present in such systems only as a result of interfacial tension fluctuations due to temperature effects.

The magnitude of temperature gradients, that can be theoretically expected from the heat of solution, was first determined by solving the equations of diffusion considering the presence of a heat source at the interface due to the heat of solution and of continuous heat production due to the heat of dilution in the bulk. The development of the treatment is presented in chapter 3.

A linearised stability analysis of the small perturbation type is applied to the temperature, concentration and velocity field in chapter 4. Stability criteria are obtained from the characteristic equation and in chapter 5 the derived predictions are compared with experimental observations for a number of selected systems.

CHAPTER 2

LITERATURE SURVEY

The literature relevant to this work is classified under two headings: experimental observations and mathematical analysis of instability.

2.1 Experimental observations

In 1855, Thomson(1) described spontaneous interfacial movements in a paper entitled: "On certain curious motions observable at the surface of wine and other alcoholic liquours" and interpreted the phenomena in terms of local changes of "the tensile force". In 1865, Marongoni(2) published his observations on the spreading of drops of one liquid on the surface of another. After Luedtge(3) and Mensbrugghe(4) reported similar observations without mentioning his work, Marangoni claimed priority for it in another publication(5) and Thomson's work passed unnoticed. Since then the phenomena of surface tension-driven movements are known as the Marangoni effect.

Numerous observations and experiments on spontaneous interfacial activity originated under different conditions have been reported afterwards. Scriven and Sternling(6) published a very interesting review on "The Marangoni effects" covering the period 1855-1960 (81 references).

Ward and Brooks(7) were the first to describe in detail the interfacial agitation accompanying mass transfer across the interface and explained it in terms of the effect of the heat of solution on the physical properties at the interface. In 1959, Sternling and Scriven(8) presented a mathematical analysis of the interfacial instability originated by the transfer across the liquid-liquid interface of a ternary system. They postulated in their model that the interfacial turbulence was produced by surface tension gradients at the interface. Since 1959 the investigation on interfacial movements accompanying mass transfer has been orientated towards the verification of Sternling and Scriven criteria of instability. Sawistowski$^{(9)}$ presented a comprehensive review of Sternling and Scriven stability analysis and discussed the more recent illustrative experimental work on spontaneous interfacial convection in ternary systems. He also included a detailed description of the qualitative behaviour of the instabilities.

Ostrovskii et al$^{(10)}$ investigated experimentally the occurrence of interfacial turbulence in mass transfer under conditions of forced convection. They interpreted the phenomena from the point of view of the relationship between two energies: the free energy of the interface (H) and the mass transfer energy (M) which they defined by:

$$H = \sigma_u S_o$$

$$M = RT(1 - C_2/mC_1)$$

where σ_i is the interfacial tension at a given total concentration C_o of the transferred substance in the two phases at equilibrium, S_o is the area occupied by one mole of the transferred substance in a monolayer, C_1 and C_2 are the concentrations of the solute in the first phase (original solution) and the second (receiving) phase when interfacial turbulence appears, m is the distribution coefficient, T the absolute temperature and R is the universal gas constant.

The hypothesis put forward to account for the appearance of free surface convection were:

(i) at the instant when turbulence arises the determining resistance is the free energy of the interface,

(ii) interfacial turbulence occurs when $M/H > 1$

The results for 19 ternary systems are in agreement with the two hypotheses.

A type of instability different from the Marangoni effect may be originated by buoyancy forces. Sawistowski and Austin(11) analysed all the possible combinations of density and direction of transfer and their effects on the gravitational stability of the interface. Their conclusions are presented in table 2.1, where ρ is the density, subscripts s, A and B refer to solute, upper phase and lower phase respectively. In their experimental work they found anomalous effects due to volume contraction on mixing .

TABLE 2.1

GRAVITATIONAL STABILITY

Relative value of solute density	Direction of transfer	Side A of the interface	Side B of the interface
$\rho_s < \rho_A < \rho_B$	A → B	stable	stable
	B → A	unstable	unstable
$\rho_A < \rho_s < \rho_B$	A → B	unstable	stable
	B → A	stable	unstable
$\rho_A < \rho_B < \rho_s$	A → B	unstable	unstable
	B → A	stable	stable

The interaction between density gradients and interfacial tension-driven instabilities was investigated experimentally by Berg and Morig(12). They concluded that "when density forces were stabilising in a phase, interfacial convection was confined to a narrow zone adjacent to the interface(1). When according to the Sternling - Scriven criteria of stability convection patterns should have been present, they appeared usually in form or roll cells which were dampled and regenerated. When density forces were de-stabilising in a phase the movements penetrated deeply and the convection pattern could not be observed.

2.1.1 Instabilities in binary systems

Merson and Quinn(13) studied mass transfer in binary systems with solute diffusing into a radially moving interface. In their experiments they worked with unsaturated phases so that mass transfer occurred simultaneously in both directions. They observed structured turbulence in the interface of the system isobutanol-water. Presaturating the water phase with isobutanol had no effect on the turbulence but saturation of the alcohol terminated the activity. They interpreted the phenomena in terms of the Marangoni effect and suggested that the interfacial tension gradient could be caused either by a concentration gradient or by a temperature gradient. In a binary system a concentration gradient independent of temperature could only exist if the interphase was not at equilibrium and the temperature gradient could be originated by thermal effects due to the heat of solution. The authors considered this the more probable cause of the Marangoni instabilities.

Using the schlieren technique(9), Austin, Ying and Sawistowski(14) investigated binary systems for the presence of interfacial instability. The schlieren object was a pendant drop of one phase suspended in the other. The systems were classified in three groups according to the intensity of the movements:

(i) stable systems: the regime of mass transfer is diffusional,

(ii) unstable systems - weak instabilities: rippling and deformation of the diffusional layer are observed, the movements in the interfacial layers are slow,

(iii) unstable systems - strong instabilities: violent movements are observed at the interface (the interfacial turbulence is similar to that observed in some ternary systems).

They suggested that equilibrium may not be established instantaneously at the interface and consequently the dynamic interfacial tension could be a critical variable during the relaxation time of the interface. Heat effects due to heat of solution were also considered a possible cause of the phenomena. Sawistowski and Austin(11) extended the investigations to 33 systems. In addition they found that the systems ethyl acetate-water and methyl acetate-water showed gravitational instability due to volumecontraction on mixing of the organic phase in the aqueous phase.

Ying and Sawistowski(16) investigated the behaviour of a flat interface of 46 partially miscible binary systems, shortly after contacting the phases. The observations were conducted in a schlieren field. They employed a vertical cell for observations in a plane normal to the interface and a horizontal cell for observations in the plane of the interface. From these investigations they reported a classification of the systems into 5 categories according to the intensity of the movements: a) interfacial turbulence, b) eruptions, c) convection cells, d) streaks or stripes and e) diffusional transfer, in decreasing order of intensity. They also found that the intensity of the interfacial turbulence in a given system is proportional to the driving force. From the 46 systems Ying and Sawistowski investigated 12 for directional effects by presaturating one of the phases. The results showed that directional effects exist in a number of systems. The system acetylacetone is a remarkable example in that the most intense instability sets in when acetylacetone is transferred to water and the interface remains stable when water is transferred into acetylacetone. Their study of dynamic interfacial tension showed that the interfacial tension at short times of exposure in the system acetylacetone-water seemed to be higher for the transfer of the organic liquid into water than for no transfer or transfer of water into acetylacetone.

2.2 Mathematical analysis of stability

The literature on the mathematics analysis of surface tension-driven instabilities may be divided into two groups: stability analysis of thin liquid layers under a vertical temperature gradient and behaviour of the liquid-liquid interface when mass transfer is taking place from one phase to the other. Since the present work is related to simultaneous heat and mass transfer the more representative papers in each groups will be mentioned.

2.2.1 Temperature induced convective flows

Under certain conditions steady state cellular patterns may be observed in thin layers heated from below or cooled from above by evaporation. The first systematic experiments were carefully carried out by Bénard(17,18) who worked with open liquid layers of spermaceti, about 1 mm. deep, heated from below. Bénard found that a critical temperature gradient had to be reached for the pattern to appear. Bénard cells were first mathematically studied by Rayleigh(20) who employed a linearized stability analysis based on the assumption that the surface movements were originated by density stratification. Rayleigh's analysis explained some characteristics of the motion and arrived at the conclusion that a certain value of a dimensionless group relating viscous to buoyancy forces (now known as Rayleigh number) had to be exceeded before fluid motion occurred. The theory was not in very good quantitative agreement with Bénard's critical gradient.

Jeffreys(21,22) and Low(23) developed a similar analysis using different boundary conditions. In these early theories the cells were assumed, for simplicity, rectangular. Later, Pellew and Southwell(24) showed how to take into account other shapes of cell wall, including the case of hexagonal cells. The theory seems to be in good agreement with experimental results for layers of about 1 cm.(46). A concise review of these treatments is given by Lin(25).

From his experimental work Block(26) concluded that cellular convection pattern could be induced by surface tension forces. Later, Pearson(27) studied the stability of a thin liquid layer with a free upper boundary and a fixed boundary heated from below. He applied to the system a perturbation analysis similar to that developed by Rayleigh(20) and Jeffreys(22) but assuming that surface tension forces rather than buoyancy forces generated the surface movements. He found that for instabilities to set in a certain value of a dimensionless number relating the destabilizing surface tension forces to the stabilizing viscous forces has to be exceeded. The critical value of this number, now called Marangoni number, is in good agreement with Bénard's experiments. Pearson suggested that in very thin layers the controlloing destabilizing force is the variation of surface tension with temperature, while in thicker layers buoyancy forces are more likely to be the controlloing destabilizing factor.

In Pearson's analysis the upper surface was considered rigid. Scriven and Sternling(28) extended the analysis to include a flexible free boundary and surface viscosity.

They found that flexible surfaces are unstable over a wider rage of parameters than it is found for a flat interface. They also found that surface viscosity exerts a stabilising influence.

Nield(29) made a theoretical investigation of convective stability in a fluid layer with a coupled density and interfacial tension driving force. Cabelli and de Vahl Davis(30) solved numerically the equations of mass, momentum and energy conservation for a linear temperature profile incorporating density and surface tension effects. They found that when both effects are present there is a certain combination of Marangoni and Rayleigh numbers that must be exceeded for instabilities to set in and that surface tension effects encourage density movements when the surface tension is a decreasing function of temperature.

Vidal and Acrivos(31) extended Pearson's analysis to include non-linear temperature profiles. They postulated that the rate of growth of an unstable disturbance will be much greater than the time rate of change of the conductive temperature profile. In addition to this standard "frozen" assumption they approximated the non-linear profile by two straight lines. Their assumption that the velocity component normal to the surface vanishes at the effective thermal depth implies that the thickness of the thermal boundary layer is greater or equal to the thickness of the velocity boundary layer. Consequently, their model would not be adequate for liquids with Prandtl number greater than one. The results of the Vidal and Acrivos' analysis show that non-linear temperature profiles "can increase the magnitude of the Marangoni number at the onset of instability by several orders of magnitude from that predicted by classical stability theory using a linear profile". They found good agreement with their experimental results.

Morton(32) and Lick(33) studied the stability of liquid layers with time-dependent heating. They considered density-driven disturbances and assumed that the rate of change of the temperature profile is small compared with the growth rate of the disturbance (quasi-static assumption). This assumption is invalid near the onset of instability. Foster(34) avoided this assumption by using an initial-value approach. The range or validity of the quasi-static assumption was studied by Robinson(35) in a semi-infinite medium. His results are in good agreement with those calculated by Foster.

2.2.2 Concentration induced convective flows

Sternling and Scriven(8) were the first to apply stability analysis to the study of interfacial activity accompanying mass transfer in a ternary liquid-liquid system. They described the mechanism of interfacial convection in terms of the Marangoni effect and applied perturbation analysis to a model consisting of two non-equilibrated media in contact along a plane interface. The system was assumed to be in steady state and the interface a rigid plane. The concentration of solute in each phase was taken to be small enough for the fluid properties to be considered uniform and constant. Their analysis suggests that interfacial instability is usually promoted by:

"(i) Solute transfer out of the phase of higher viscosity,

(ii) Solute transfer out of the phase in which diffusivity is lower,

(iii) large differences in kinematic viscosity and solute diffusivity between the two phases,

(iv) steep concentration gradients near the interface,

(v) interfacial tension highly sensitive to solute concentration,

(vi) low viscosities and diffusivities in both phases,

(vii) absence of surface active agents, and

(viii) interfaces of large extent.

Marsh, Sleicher and Heideger(36) extended Sternling and Scriven's analysis to include time-dependent concentration gradients. In their treatment they used Sternling and Scriven's solution for the equation of motion, which implies that the size and rate of growth of the disturbance are independent of time or that a quasi-static assumption is adopted. They do not establish any difference between the time after contacting the phases and the time after the onset of the perturbation. This implies the wrong assumption that the variation of concentration profiles with time does not affect either the size or the growth rate of the disturbance. Their results are in qualitative agreement with Sternling and Scriven criteria of stability, except for the influence of the relative value of diffusivity. They found that solute transfer out of the phase of higher diffusivity is a destabilising factor.

Gross and Hixon(37) studied the Marangoni instability with unsteadydiffusion in the undisturbed state including an interfacial resistance to mass transfer. They present a solution in series for the time-dependent perturbed temperature profile. The infinite series representing the characteristic equation is truncated for long periods of contact. They found their criteria of stability to be the same as those of Sternling and Scriven(8). From numerical results for conditions approaching steady state they reported a variation of the size and growth rate of the disturbance with time from the onset of perturbation.

CHAPTER 3

TIME-DEPENDENT CONCENTRATION AND TEMPERATURE PROFILES IN BINARY SYSTEMS

In most cases the process of mixing of two liquids is accompanied by release or absorption of heat. Consequently, when two liquids are gently brought into contact to form a horizontal interface, a temperature profile will be established in each phase in addition to a concentration gradient. Since the amount of heat evolved or absorbed depends on the amount of solute dissolved, the magnitude of the temperature gradient will be determined not only by the physical properties of the media involved but also by the magnitude of the mass flux. If the usual assumption is then made that the phases are in equilibrium at the interface, a change in temperature there will cause a corresponding change in concentration which, in turn, will produce a modification of the temperature profile. Therefore, heat and mass transfer are closely related and have to be considered simultaneously.

3.1 Description of the Model

The model to be studied consists of two semi-infinite media in contact along a plane interface. Equilibrium concentration exists at the interface and changes in temperature are followed instantaneously by corresponding changes in concentration. Mass and heat released by the mixing process are transferred through both phases in the direction normal to the interface.

The concentration of the diffusing liquids is low and temperature gradients are small so that fluid properties may be considered constant and buoyancy effects, mass flux due to thermal diffusion and Dufour energy flux can be neglected.

3.2 Mathematical Formulation

Figure 3.1 shows a schematic representation of the system. According to the assumptions made in the model, the equation of conservation of mass reduces to Fick's second law of diffusion.

$$\frac{\partial C_A}{\partial t} - D_A \frac{\partial^2 C_A}{\partial x^2} = 0 \;; \quad t > 0; \quad x \geqslant 0 \qquad (3.1)$$

$$\frac{\partial C_B}{\partial t} - D_B \frac{\partial^2 C_B}{\partial x^2} = 0 \;; \quad t > 0; \quad x \leqslant 0 \qquad (3.2)$$

where C_A is the concentration of the solute B in phase A, C_B the concentration of solute A in phase B, D_A is the diffusivity of liquid B in phase A and D_B is the diffusivity of A in B.

The energy equation is:

$$\frac{\partial T_A}{\partial t} - K_A \frac{\partial^2 T_A}{\partial x^2} = \frac{S_A}{\rho_A C_{PA}} \;; \quad t > 0 \;; \quad x \geqslant 0 \qquad (3.3)$$

$$\frac{\partial T_B}{\partial t} - K_B \frac{\partial^2 T_B}{\partial x^2} = \frac{S_B}{\rho_B C_{PB}} \;; \quad t > 0 \;=\; x \leqslant 0 \qquad (3.4)$$

where S_A and S_B are the volumetric rates of production of thermal energy by solution of B in phase A and of A in phase B respectively. Figure 3.2 shows the enthalpy-concentration diagram for a partially miscible system. If the solution were ideal, the isotherm relating enthalpy to concentration would be a straight line joining points

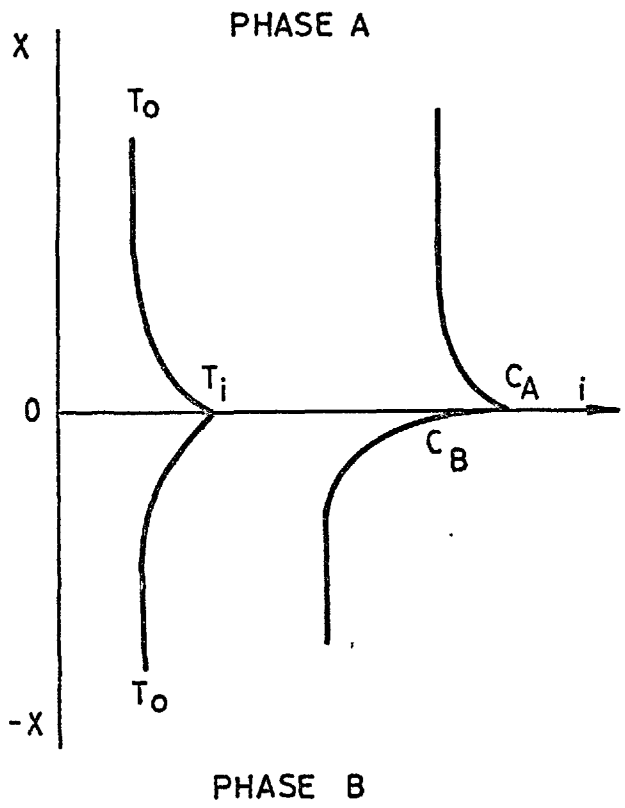


FIG. 3·1 MODEL REPRESENTATION

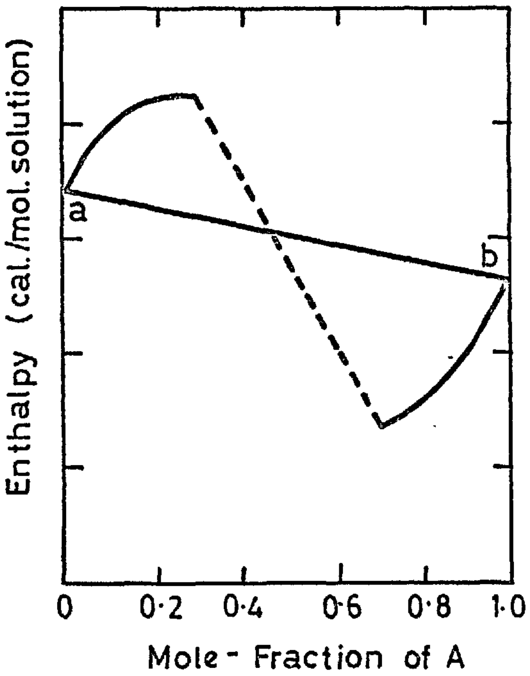


FIG. 3·2 ENTHALPY - CONCENTRATION DIAGRAM

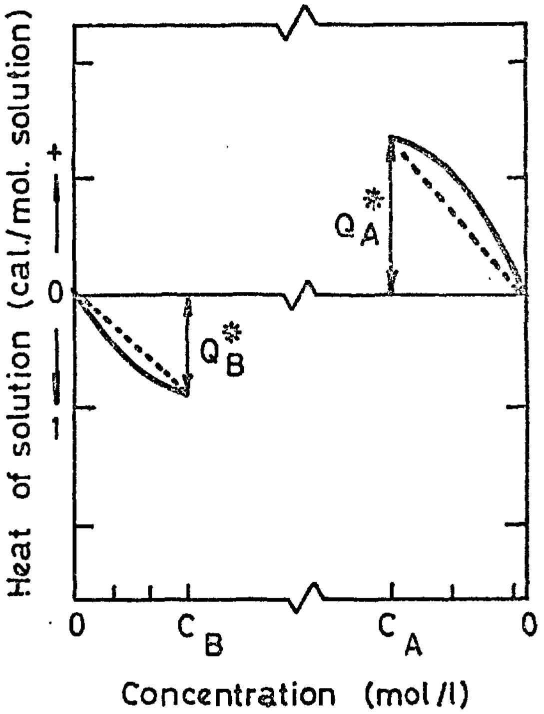


FIG. 3·3 HEAT OF SOLUTION-CONCENTRATION

a and b. The difference between the values of the enthalpy of the solution on the real curve and that on the ideal straight line for a given concentration, is the integral heat of solution per mole of solution Q. This system, like many other partially miscible systems, has positive heat of solution in one phase and negative in the other.

The amount of heat released during the mixing process depends on the change in concentration. If C is the concentration at a plane x of the model under study and Q is the corresponding integral heat of solution, the volumetric rate of heat production, positive or negative, at that plane will be:

$$S = \frac{\rho}{\underline{M}} \left(\frac{\partial Q}{\partial C}\right)_C \frac{\partial C}{\partial t} \qquad (3.5)$$

where ρ is the density of the solution at the concentration C and $\underline{M}$ is the molecular weight of the solution at the same concentration.

On substitution of equation (3.5) into equations (3.3) and (3.4):

$$\frac{\partial T_A}{\partial t} - K_A \frac{\partial^2 T_A}{\partial x^2} = \frac{1}{\underline{M}_A C_{PA}} \frac{\partial Q_A}{\partial C_A} \frac{\partial C_A}{\partial t} \qquad (3.6)$$

$$\frac{\partial T_B}{\partial t} - K_B \frac{\partial^2 T_B}{\partial x^2} = \frac{1}{\underline{M}_B C_{PB}} \frac{\partial Q_B}{\partial C_B} \frac{\partial C_B}{\partial t} \qquad (3.7)$$

These equations cannot be solved analytically unless some simplifications are made. According to the characteristics of the model, not only K but also $\underline{M}$ and C_P will be assumed independent of C. The second simplification to the right hand side of both equations concerns the variation of the heat of solution with concentration. Figure 3.3 shows the integral heat of solution - concentration diagram for the same system. Since for partially miscible pairs the interval of possible concentrations in each phase is small at temperatures not too close to the critical solution temperature, it is justified to linearise the heat of solution vs. concentration curve over the solubility range. This assumption reduces the curve to the dotted straight line shown in Figure 3.3, and the term $\frac{\partial Q}{\partial C}$ to a constant. As the heat of solution at C = 0 is equal to zero, the equation of the straight line is:-

$$Q = Q_r \, C \tag{3.8}$$

where $Q_r = \frac{\partial Q}{\partial C} = \text{const.}$

Except for $\frac{\partial C_A}{\partial t}$ and $\frac{\partial C_B}{\partial t}$, all the terms on the right-hand side of equations (3.6) and (3.7) are now constant and analytical integration is possible.

For further treatment it is more convenient to change the variables C and T to the following:

$$\Delta = C - C_o \tag{3.9}$$

$$\Theta = T - T_o \tag{3.10}$$

where C_o and T_o are the initial concentration and temperature respectively.

Calling:

$$E = Q_r/\underline{M}C_o \tag{3.11}$$

and substituting equations (3.9), (3.10), and (3.11) into equations (3.1), (3.2), (3.6) and (3.7), the following expressions are obtained:

$$\frac{\partial \Delta_A}{\partial t} - D_A \frac{\partial^2 \Delta_A}{\partial x^2} = 0 \qquad (3.12)$$

$$\frac{\partial \Delta_B}{\partial t} - D_B \frac{\partial^2 \Delta_B}{\partial x^2} = 0 \qquad (3.13)$$

$$\frac{\partial \otimes_A}{\partial t} - K_A \frac{\partial^2 \otimes_A}{\partial x^2} = E_A \frac{\partial \Delta_A}{\partial t} \qquad (3.14)$$

$$\frac{\partial \otimes_B}{\partial t} - K_B \frac{\partial^2 \otimes_B}{\partial x^2} = E_B \frac{\partial \Delta B}{\partial t} \qquad (3.15)$$

3.3 Initial and boundary conditions

The initial conditions are:

$$\left.\begin{array}{llll} \text{(i)} & \Delta_A = 0 & ; & x \geqslant 0 \\ \text{(ii)} & \Delta_B = 0 & ; & x \leqslant 0 \\ \text{(iii)} & \otimes_A = 0 & ; & x \geqslant 0 \\ \text{(iv)} & \otimes_B = 0 & ; & x \leqslant 0 \end{array}\right] \quad t \leqslant 0$$

The boundary conditions at infinity are:

(v) $\Delta_A = 0 \quad ; \quad x = \infty$

(vi) $\Delta_B = 0 \quad ; \quad x = -\infty$

(vii) $\otimes_A = 0 \quad ; \quad x = \infty$

(viii) $\otimes_B = 0 \quad ; \quad x = -\infty$

At the interface the two phases are at the same temperature:

(ix) $\theta_A = \theta_B$; $x = 0$

Since the expected temperature gradients are small, the variation R of interfacial concentration with temperature may be assumed linear between the initial and final temperatures at the interface:

$$R = \frac{\partial C}{\partial T} = \frac{C^* - C_o^*}{Ti - T_o} = \text{const} \qquad (3.16)$$

where C^* is the saturation concentration at Ti, the temperature at the interface, and C_o^* is the saturation concentration at the initial temperature. Hence boundary conditions (x) and (xi) become:

(x) $\Delta_A^* = R_A\theta_A + C_{AO}^* - C_{AO}$; $x = 0$

(xi) $\Delta_B^* = R_B\theta_B + C_{BO}^* - C_{BO}$; $x = 0$

where

$$\Delta^* = C^* - C_o$$

The last boundary condition is obtained from conservation of heat at the interface. The amount of heat released at the interface per unit interfacial area and per unit time is

$$Q_T = - D_A \left.\frac{\partial C_A}{\partial x}\right|_{x=o} Q_A^o + D_B \left.\frac{\partial C_B}{\partial x}\right|_{x=o} Q_B^o \qquad (3.17)$$

where $$Q^o = Q_r \frac{\rho}{\underline{M}} \qquad (3.18)$$

is the heat of solution per mole of solute.

The heat released at the interface is transferred to both phases. Hence, combining equation (3.17) with Fourier's law of heat conduction, boundary conditions (xii) is, in terms of variables defined by expressions (3.9) and (3.10),:

(xii) $$- D_A \frac{\partial \Delta_A}{\partial x} Q_A^o + D_B \frac{\partial \Delta_B}{\partial x} Q_B^o = - k_A \frac{\partial \theta_A}{\partial x} + k_B \frac{\partial \theta_B}{\partial x} \quad ;$$

$$x = 0$$

where k is the thermal conductivity.

3.4 Solution of the diffusion equations

The four partial differential equations are solved by applying the Laplace transform method. The transformed equations are:

$$- \Delta_A(o) + s \, \bar{\Delta}_A - D_A \frac{d^2 \bar{\Delta}_A}{dx^2} = 0 \qquad (3.19)$$

$$- \Delta_B(o) + s \, \bar{\Delta}_B - D_B \frac{d^2 \bar{\Delta}_B}{dx^2} = 0 \qquad (3.20)$$

$$- \theta_A(o) + s \, \bar{\theta}_A - K_A \frac{d^2 \bar{\theta}_A}{dx^2} = E_A \left(- \Delta_A(o) + s\bar{\Delta}_A \right) \qquad (3.21)$$

$$- \theta_B(o) + s \, \bar{\theta}_B - K_B \frac{d^2 \theta_B}{dx^2} = E_B \left(- \Delta_B(o) + s\bar{\Delta}_B \right) \qquad (3.22)$$

From initial conditions (i) to (iv), equations (3.19) to (3.22) become:

$$\frac{d^2 \bar{\Delta}_A}{dx^2} - \frac{s}{D_A} \bar{\Delta}_H = 0 \qquad (3.23)$$

$$\frac{d^2 \bar{\Delta}_B}{dx^2} - \frac{s}{D_B} \bar{\Delta}_B = 0 \qquad (3.24)$$

$$\frac{d^2 \bar{\theta}_A}{dx^2} - \frac{s}{K_A} \bar{\theta}_A = - \frac{s}{K_A} E_A \bar{\Delta}_A \qquad (3.25)$$

$$\frac{d^2 \bar{\theta}_B}{dx^2} - \frac{s}{K_B} \bar{\theta}_B = - \frac{s}{K_B} E_B \bar{\Delta}_B \qquad (3.26)$$

The solutions of these equations are:

$$\bar{\Delta}_A = C_1 \exp(\sqrt{s/D_A}\; x) + C_2 \exp(-\sqrt{s/D_A}\; x) \qquad (3.27)$$

$$\bar{\Delta}_B = C_3 \exp(\sqrt{s/D_B}\; x) + C_4 \exp(-\sqrt{s/D_B}\; x) \qquad (3.28)$$

$$\bar{\otimes}_A = C_5 \exp(\sqrt{s/K_A}\; x) + C_6 \exp(-\sqrt{s/K_A}\; x) + \frac{E_A}{1-K_A/D_A}\,\bar{\Delta}_A \qquad (3.29)$$

$$\bar{\otimes}_B = C_7 \exp(\sqrt{s/K_B}\; x) + C_8 \exp(-\sqrt{s/K_B}\; x) + \frac{E_B}{1-K_B/D_B}\,\bar{\Delta}_B \qquad (3.30)$$

The transformed boundary conditions are:

(v) $\bar{\Delta}_A = 0 \quad ; \quad x = \infty$

(vi) $\bar{\Delta}_B = 0 \quad ; \quad x = -\infty$

(vii) $\bar{\otimes}_A = 0 \quad ; \quad x = \infty$

(viii) $\bar{\otimes}_B = 0 \quad ; \quad x = -\infty$

(ix) $\bar{\otimes}_A = \bar{\otimes}_B \quad ; \quad x = 0$

(x) $\bar{\Delta}_A = R_A\,\bar{\otimes}_A + (C_{AO} - C_{AO})/s \quad ; \quad x = 0$

(xi) $\bar{\Delta}_B = R_B\,\bar{\otimes}_B + (C_{BO} - C_{BO})/s \quad ; \quad x = 0$

(xii) $-D_A(d\bar{\Delta}_A/dx)Q_A^O + D_B(d\bar{\Delta}_B/dx)Q_B^O = -k_A(d\bar{\otimes}_A/dx) + k_B(d\bar{\otimes}_B/dx) \quad ; \quad x = 0$

Using conditions (v), (vi), (vii) and (viii), equations (3.19), (3.20), (3.21) and (3.22) become:

$$\bar{\Delta}_A = C_2 \exp(-\sqrt{s/D_A}\; x) \qquad (3.31)$$

$$\bar{\Delta}_B = C_3 \exp(\sqrt{s/D_B}\; x) \qquad (3.32)$$

$$\bar{\Theta}_A = C_6 \exp\left(-\sqrt{S/K_A}\, x\right) + \left(E_A/(1-K_A/D_A)\right) \bar{\Delta}_A \qquad (3.33)$$

$$\bar{\Theta}_B = C_7 \exp\left(\sqrt{S/K_B}\, x\right) + \left(E_B/(1-K_B/D_B)\right) \bar{\Delta}_B \qquad (3.34)$$

The constant C_2, C_3, C_6 and C_7 are determined from the four remaining boundary conditions:

$$C_2 = \frac{1}{s} \frac{(E_B F_B/m)(R_A(C^{*}_{BO}-C_{BO})-R_B(C^{*}_{AO}-C_{AO})) + r\sqrt{L_A}(1+1/hm)(C^{*}_{AO}-C_{AO})}{r(\sqrt{L_A}(1+1/hm) - E_A R_A F_A) - E_B R_B F_B/m}$$

where $L = \frac{K}{D}$ (Lewis number) (3.35)

$$F = \frac{1 + 2\sqrt{L}}{1 + \sqrt{L}}$$

$$r^2 = \frac{D_A}{D_B}$$

$$h^2 = \frac{K_A}{K_B}$$

$$m = \frac{\rho_A C_{PA}}{\rho_B C_{PB}}$$

On writing equation (3.5) as

$$C_2 = \frac{1}{s} C^1{}_2 \qquad (3.36)$$

constants C_4, C_6 and C_8 become:

$$C_3 = \frac{1}{s} (C^1{}_2 + R_C (C^{*}_{BO} - C_{BO}) - (C^{*}_{AO} - C_{AO}))/R_C$$

$$= \frac{1}{s} C^1{}_3 \qquad (3.37)$$

where $R_C = R_A/R_B$

$$C_6 = \frac{1}{s} ((1-E_A R_A/(1-L_A) c^1{}_2 - (C^*_{AO}-C_{AO}))/R_A = \frac{1}{S} \; c^1{}_6 \qquad (3.38)$$

$$C_7 = (1 - E_B R_B/(1-L_B) \left[c^1{}_2 + R_C \; (C^*_{BO} - C_{BO}) - C^*_{AO} - C_{AO} \right]$$

$$/(R_C R_B s) - (C^*{}_{BO} - C_{BO})/R_B s = \frac{1}{s} \; c^1{}_7$$

(3.39)

Combining equations (3.36) to (3.39) with equations (3.31) to (3.34):

$$\bar{\Delta}_A = \frac{1}{s} \; c^1{}_2 \exp \left(- \sqrt{s/D_A} \; x\right) \qquad (3.40)$$

$$\bar{\Delta}_B = \frac{1}{s} \; c^1{}_3 \exp \left(\sqrt{s/D_B} \; x\right) \qquad (3.41)$$

$$\bar{\Theta}_A = \frac{1}{s} \; c^1{}_6 \exp \left(- \sqrt{s/K_A} \; x\right) + E_A/(1-L_A) \; \bar{\Delta}_A \qquad (3.42)$$

$$\bar{\Theta}_B = \frac{1}{s} \; c^1{}_7 \exp \left(\sqrt{s/K_B} \; x\right) + E_B/(1-L_B) \; \bar{\Delta}_B \quad , \qquad (3.43)$$

The inverse transform of these equations, on reverting to the original notation (equations (3.9) and (3.10)), are

$$C_A - C_{AO} = c_2{}^1 \text{ erfc } (x/2 \sqrt{D_A t}) \qquad (3.44)$$

$$C_B - C_{BO} = c^1{}_3 \text{ erfc } (-x/2\sqrt{D_B t}) \qquad (3.45)$$

$$T_A - T_{AO} = c^1{}_6 \text{ erfc } (x/2\sqrt{K_A t}) + (E_A/(1-L_A))\, c^1{}_2 \text{ erfc } (x/2\sqrt{D_A t})$$

(3.46)

$$T_B - T_{BO} = c^1{}_7 \text{ erfc } (-x/2\sqrt{K_B t}) + (E_B/(1-L_B))c^1{}_3 \text{ erfc } (-x/2\sqrt{D_B t})$$

(3.47)

The four constants in these equations involve the heat and mass transport properties together with the heat of solution in each phase, the rate of variation of equilibrium concentration with temperature, the density, the heat capacity, the equilibrium concentration at the initial temperature, and the initial temperature and concentration. Equations (3.44) and (3.45) are of the same form as the equation for the concentration profile when heat effects are absent except for the difference in the constants. When the change of equilibrium concentration with temperature over a small temperature interval is equal to zero in both phases, constants $C_2{}^1$ and $C_3{}^1$ become equal to $C^*_{AO}-C_{AO}$ and $C^*_{BO}-C_{BO}$ respectively and equations (3.44) and (3.45) reduce to the solution of the diffusion equation for ideal solution. This means that mass transfer is affected only by the heat flux through the change in interfacial concentration with temperature. As for the temperature profiles, which are a consequence of non-ideality in the mixing process, their dependence on mass flux is more complex. The terms containing constants $C^1{}_6$ and $C^1{}_7$ express the departure from the initial temperature due to diffusion of the heat generated at the interface, at a point x after a time t. The terms affected by constants $C^1{}_2$ and $C^1{}_3$ account for the differential heat of solution released by the change of concentration at the same point.

Figure 3.4(a) and (b) shows the temperature profiles for the system methyl ethyl ketone when water is transferred from the saturated water phase to pure methyl ethyl ketone.

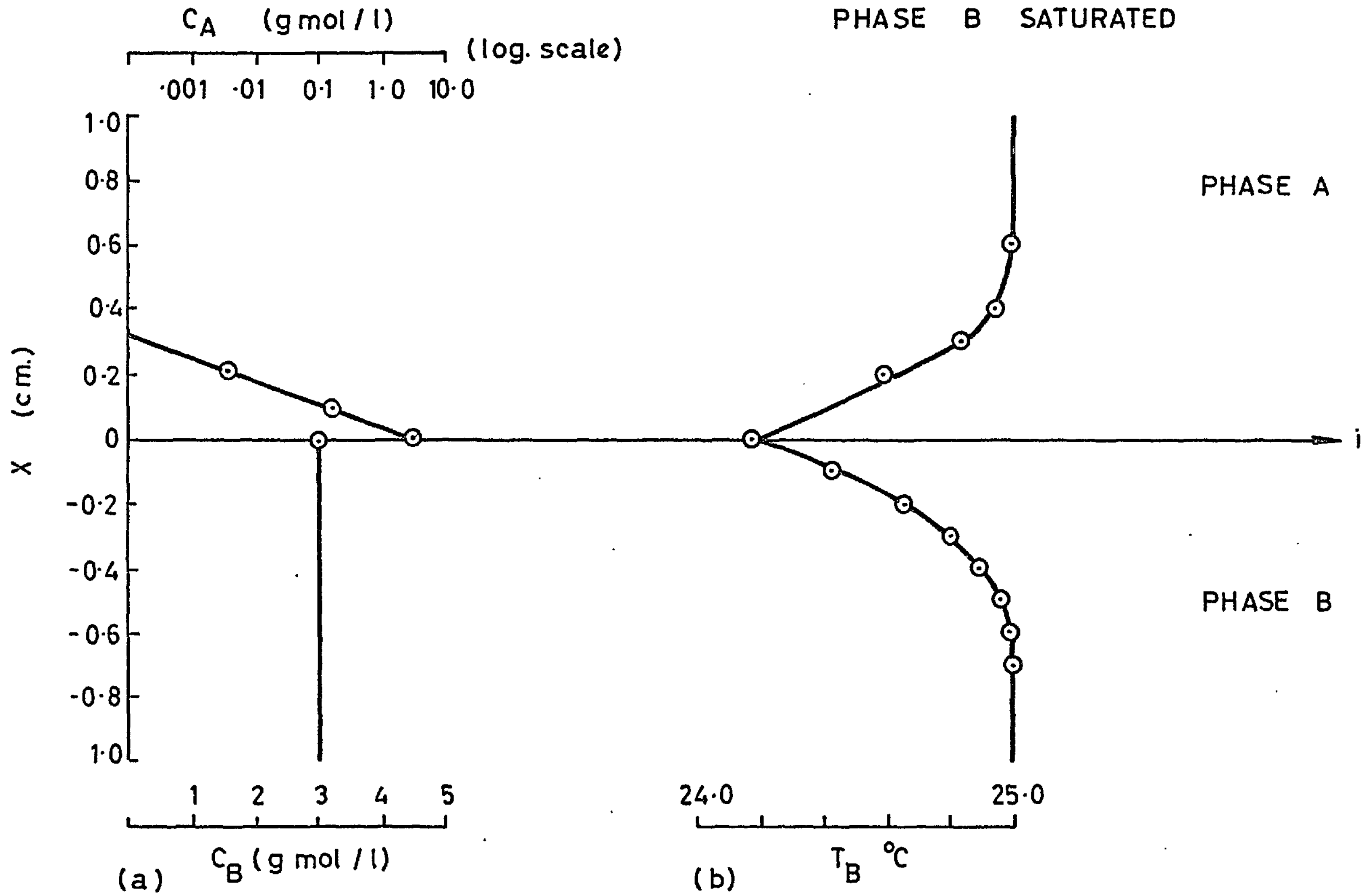


FIG. 3·4 CONCENTRATION AND TEMPERATURE PROFILES IN THE SYSTEM METHYL ETHYL KETONE - WATER

The profiles have been calculated with equations (3.44), (3.46) and (3.47) at 30 seconds after contacting the phases. The physical properties of the system are presented in chapter 5 and Appendix B.

CHAPTER 4.

STABILITY ANALYSIS

The study of mass transfer with thermal effects discussed in Chapter 5 shows that temperature gradients of a certain magnitude can be expected on contacting two partially miscible liquids. The system methyl ethyl ketone-water for which, as an example, theoretical temperature and concentration profiles were calculated, may be considered a representative water-organic solvent system from the thermodynamic point of view. The theoretical temperature gradients obtained for this system are of the same order of magnitude as the critical temperature gradient: that is the gradient at the onset of convection, as measured by Vidal and Acrivos (31) in their study of the stability of shallow evaporating layers of propyl alcohol. Ying and Sawistowski (16) investigated the stability of binary systems under conditions in which the thickness of the layers was too large to be considered a controlling variable. They found that unstable systems develop turbulence at the interface immediately after the phases are brought into contact, and the intensity of turbulence was a function of the mass transfer driving force. These observations suggest that although the thickness of the layers may be large, instabilities set in when the penetration depth of the temperature profile is still small. According to Pearson(27), when the thickness of evaporating layers is "as small as 1 mm, the onset of cellular motion could confidently be attributed to surface tension rather than to buoyancy". In the case of binary liquids systems the equation for the temperature profile developed in Chapter 3 establishes that the temperature at the interface does not change with time. Since the depth of penetration of the temperature profile increases with time, the temperature gradient decreases in absolute value. So, even when the thermal thickness of the layers is large enough for buoyancy forces due to thermal effects to become important, the temperature gradient is in general too small to produce instability of that type. There may be buoyancy forces produced by changes in specific volume of the solutions with mixing, but these forces do not depend on temperature gradients of the magnitude considered.

The previous considerations lead to the conclusion that interfacial tension forces are more likely to produce instabilities at the interface of binary liquid systems than buoyancy forces. Therefore, the stability of the interface will be studied with respect to interfacial tension disturbances only.

4.1 Qualitative description of the mechanism of instability

In order to analyse the qualitative behaviour of the disturbed system mass transfer in only one direction will be considered. Figure (4.1a) shows schematically the system to be studied. Phase B is saturated with liquid A, so that mass transfer takes place only from phase B to phase A. The heat of solution is assumed positive, hence the temperature at the interface is higher than that in the bulk and the gradient of temperature is negative in phase A and positive in phase B. If the rate of change of interfacial tension with temperature, σ_T, is negative, a positive perturbation in the interfacial temperature will generate a local area of lower interfacial tension. Figure (4.1b)

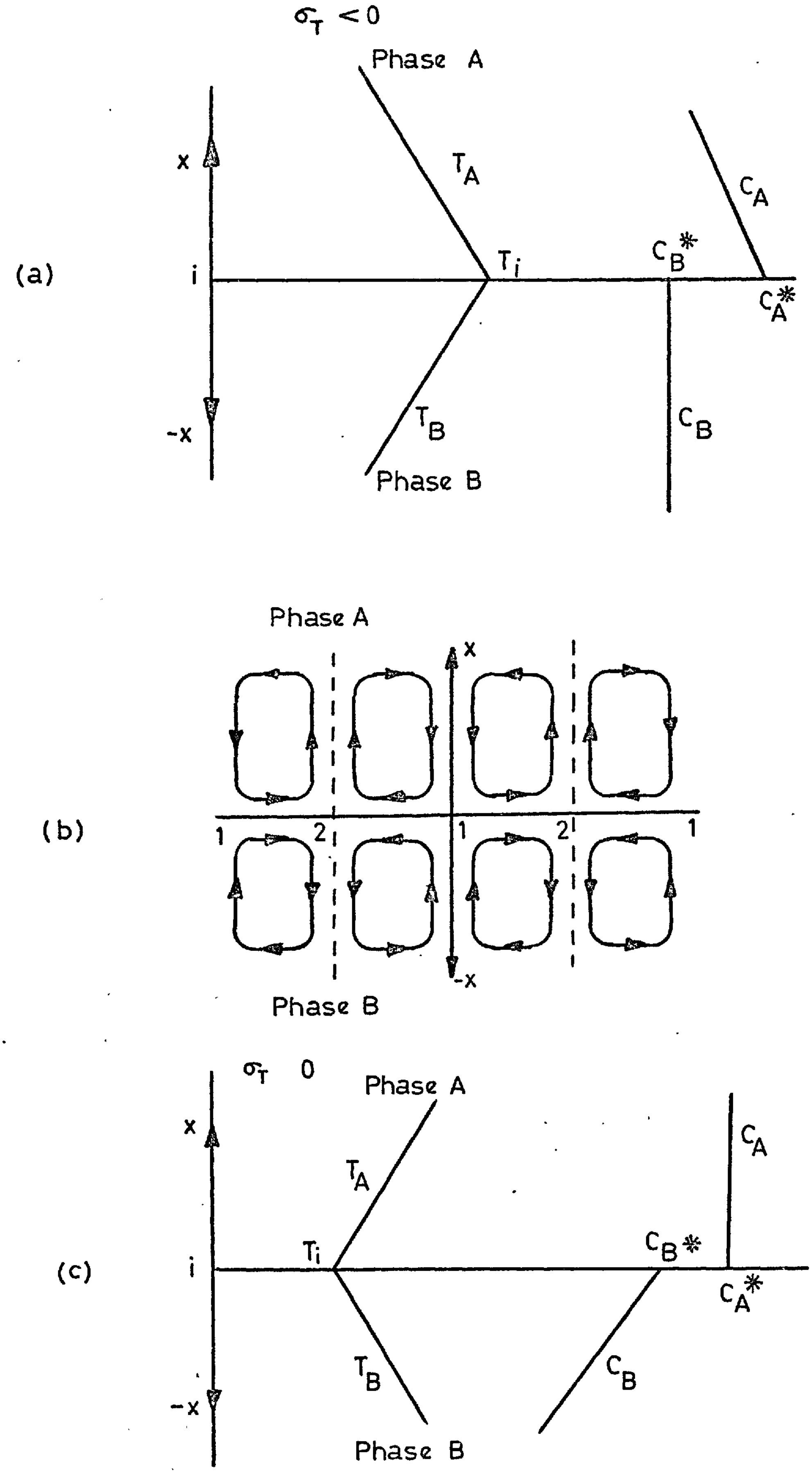


FIG. 4·1 MECHANISM OF INSTABILITY

shows the disturbed system. The temperature at points 1 is greater than the undisturbed interfacial temperature, therefore they are points of lower interfacial tension. The force system at the interface is now unbalanced and fluid at points 1 will expand according to the Marangoni principle. The movements are first parallel to the interface and then turn away into the bulk as the flow from two points 1 meet at point 2. At the same time liquid from the bulk is supplied to points 1. This liquid is at a lower temperature than the interface in both phases and lean in solute in phase A. This difference in temperature is a stabilising factor since a decrease in temperature at point 1 increases its interfacial tension. But if an element of liquid from the bulk reaches point 1 at a lower concentration than the interfacial value, an increase in mass flux will take place there and consequently, as the heat of solution is positive, there will be an increase in the heat production. The net change in temperature at points 1 is the balance between these two opposite effects. However, while the element of liquid is moving towards the interface, mass and heat transfer are taking place in order to restore the concentration and temperature profiles disrupted by the convection current. Since $K_A/D_A > 1$ for most liquids, heat transfer is faster than mass transfer and the concentration of the liquid reaching the interface will be relatively further removed from interfacial conditions than the temperature. This means that the destabilizing force will be generally stronger than the stabilizing cooling effect. Apart from the two factors already mentioned, the ratio of the kinematic viscosities in a given system also plays an important rôle. The higher the viscosity the deeper is the penetration of momentum and therefore the lower the temperature and concentration of the fluid arriving from the bulk. Hence, kinematic viscosity affects the rate of heat supply and, via mass transfer, the rate of heat production at the interface. The situation is thus similar to that discussed before and the opposing factors are again in evidence. For the case under consideration a higher viscosity of phase A is therefore expected to enhance the destabilizing effect. For mass transfer taking place in the opposite direction, that is with phase A saturated, the general behaviour of the system will be the same provided the heat of solution of A in B is also positive. However, if viscosity is higher in phase A, the heat transfer effect is controlled by phase A whereas phase B is responsible for heat generation. The net effect is thus difficult to predict qualitatively. The above analysis leads to the conclusion that systems with negative rate of change of interfacial tensions with temperature and with interface behaving as a heat source, are likely to be unstable.

For mass transfer taking place in the opposite direction, but with a negative heat of solution of A in B, the temperature gradient in phase A will be positive and that in phase B will be negative. Figure (4.1c) shows the relevant temperature and concentration profiles. When the temperature at the interface is perturbed by positive disturbances,local areas of higher temperature and therefore of lower interfacial tension will be created. The same

Marangoni movements as described before will be produced but now the liquid supplied from the bulk will be at a higher temperature and lower concentration than the interface. Consequently, the element of fluid arriving from the bulk at point 1 will supply heat but the increase in mass flux at that point will increase the rate of heat production. As this is now negative, it will tend to decrease the temperature there. Since in phase B, K_B/D_B is also greater than one, the arguments used previously apply again, that is the process is mass transfer controlled. Hence, the stabilizing effect of the increase in the mass flux will predominate causing the original disturbance to be damped. This pattern of behaviour will be affected by viscosity effects in a manner previously discussed. It may be concluded that systems with negative rate of change of interfacial tension with temperature and with interface behaving as a heat sink, are likely to be stable.

The reverse conclusions are obtained from the behaviour of systems with positive rate of change of interfacial tension with temperature. These systems are likely to be unstable when the interface acts as a heat sink and vice-versa.

For mass transfer taking place in both directions, that is if none of the phases is saturated, the signs of the temperature gradients are controlled by the net rate of heat production at the interface. The same arguments as discussed for unidirectional mass transfer apply for each phase. The reaction of the system to perturbations in interfacial temperature will depend on the balance of energy at the interface.

The above qualitative analysis of the mechanism of instability suggests that the stability of the disturbed system depends on the sign of the temperature profiles, the sign of the rate of change of interfacial tension with temperature, the viscosity ratio and the direction of transfer.

4.2 Description of the model

The different mathematical approaches to the stability of surfaces to surface tension forces have been discussed in Chapter 2. Since in the systems studied the thickness of the layers does not seem to be a critical variable for the onset of instability and because of the mathematical simplifications associated with boundary conditions taken at infinity, the system will be assumed to consist of semi-infinite media.

The stability analysis involves the solution of the perturbed heat and mass diffusion equations. For the type of velocity perturbation usually applied in hydrodynamic stability analysis, the perturbed diffusion equations for the profiles represented by equations (3.44) to (3.47) have to be solved numerically. The generalisation of the Sternling and Scriven's and Person's analysis to include unsteady state conditions have shown that the stability criteria for systems with time-dependent profiles is the same as for linear profiles, but the size and the growth constant of the disturbance depend on the shape of the profile. As the purpose of this work is to predict the conditions which promote, or hinder, the onset of instability, it is therefore sufficient to conduct stability analysis on the assumption of linear profiles.

In accordance with the above discussion, it is assumed that the system consists of two semi-infinite partially miscible liquid phases in contact along an interface of infinite extent. The phases are in thermal and chemical equilibrium at the interface. In the undisturbed state the concentration and temperature profiles are linear, thus implying a steady transfer of mass and heat. The interfacial tension is assumed large enough to prevent the interface from deformations. The model has the same characteristics as that described in Chapter 3. The system is assumed to be initially undisturbed. Two-dimensional infinitesimal disturbances are then introduced and the stability of the system with respect to such disturbances investigated. If the disturbance decays the system is said to be stable; if it grows the system is unstable.

4.3 Outline of procedure

The mathematical problem may be formulated by perturbing the quiescent medium with a disturbance of a suitable kind. The resulting equation of motion will form a set of non-linear equations that can be linearised for small disturbances. The linearised equations can be solved by separating the variables. Introducing a stream function, of a form $\psi = \wp(x) \exp(i\alpha y) \exp(\beta t)$ into the linearised equation, the problem is reduced to finding the solution for $\wp(x)$. The quantity α is the wave number and β is the growth constant. The boundary conditions of the resulting differential equation of perturbation require the absence of the x-component of the disturbance velocity at the boundaries, therefore the differential equation is an eigenvalue problem for the determinations of the quantity β. The interfacial boundary condition specific to mass transfer with heat effects in binary systems will contain the variation of interfacial tension along the interface. Since interfacial tension is a function of temperature, the distribution of temperature along the y-axis has to be found for the perturbed system. This requires the solution of the perturbed heat and mass diffusion equations. On combining these solutions with the solution of the equations of motion, the characteristic equation of the system is obtained. This equation gives the relation between the growth constant, the wave number and various system properties. It establishes under which conditions the disturbance will decay or grow and which type and magnitude of instability may be expected.

4.4 Equations of motion:

The mathematical procedure applied to the hydrodynamic study of the model is similar to that developed by Sternling and Scriven (8) for the study of ternary non-equilibrated liquid-liquid systems.

For the conditions of the model the equation of motion reduces to the two-dimensional Navier-Stokes equation. In the absence of body forces this equation becomes:

$$\frac{\partial u}{\partial t} + u\,\frac{\partial u}{\partial x} + v\,\frac{\partial u}{\partial y} = -\,\frac{1}{\rho}\;\frac{\partial \overline{P}}{\partial x} + \nu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) \qquad (4.1)$$

$$\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} = -\frac{1}{\rho}\frac{\partial \overline{P}}{\partial y} + \nu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) \qquad (4.2)$$

where $\overline{P}$ is the pressure, ν the kinematic viscosity and u and v are velocity components in the direction x and y respectively. Eliminating the pressure term by cross-differentiation and assuming that the disturbance is so small that the terms of second order of smallness may be neglected (creeping flow), equations (4.1) and (4.2) simplify to the following linear equation:

$$\frac{\partial^2 v}{\partial t \partial x} - \frac{\partial^2 u}{\partial t \partial y} = \nu\left(\frac{\partial^3 v}{\partial x^3} + \frac{\partial^3 v}{\partial x \partial y^2} - \frac{\partial^3 u}{\partial x^2 \partial y} - \frac{\partial^3 u}{\partial y^3}\right) \qquad (4.3)$$

The continuity equation is:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \qquad (4.4)$$

For a potential field of velocity, the velocities may be expressed in terms of the stream function Ψ in the following way:

$$u = -\partial\Psi/\partial y \qquad v = \partial\Psi/\partial x \qquad (4.5)$$

It should be noted that in a stationary medium the steady-state velocity is zero so that u and v represent the velocity perturbations.

A stream function of the form:

$$\Psi = \wp(x)\exp(i\alpha y)\exp(\beta t) \qquad (4.6)$$

is assumed to represent a single oscillation of the disturbance. In this equation, α is a real quantity defined by the expression

$$\alpha = \frac{2\Pi}{\lambda} \qquad (4.6a)$$

where λ is the wave length of the disturbance. The quantity β is complex:

$$\beta = \beta_r + i\beta_i \qquad (4.6b)$$

where β_r is the amplification factor and β_i is the circular frequency of the partial oscillation. The amplification factor determines the degree of amplification or damping of the disturbance with time. If β_r is negative for all values of α, the system is stable. If it is positive for some values of α, the system is unstable. If $\beta_r > 0$ and $\beta_i = 0$, the instability grows in place. This type of instability is called stationary. If $\beta_i \neq 0$ and $\beta_r > 0$, oscillatory instability sets in, exhibiting temporal periodicity with period $2\Pi/\beta_i$. The case of $\beta_r = 0$ indicates marginal or neutral stability: the disturbance neither grows nor decays with time. If in addition $\beta_i = 0$, that is $\beta = 0$, the regime is referred to as neutral stationary stability and will be denoted in the subsequent development by subscipts NS. On inserting the stream function, equation (4.6), combined with the expressions (4.5) for the velocities, the time independent Orr-Sommerfeld equation for two dimensional flow is obtained:

$$\varphi'''' - 2\alpha^2\varphi'' + \alpha^4\varphi = \frac{\beta}{\nu}\,(\varphi'' - \alpha^2\varphi) \qquad (4.7)$$

where the number of primes represents the order of the derivative of with respect to x. Introduction of the dimensionless variable:

$$X = \alpha x$$

into equation (4.7) leads to:

$$\varphi'''' - 2\varphi'' + \quad = \frac{\beta}{\alpha^2 \nu} \left(\varphi'' - \varphi\right) \qquad (4.8)$$

the solution of this equation for $\beta \neq 0$ is:

$$\varphi = A_1 \exp(X) + A_2 \exp(-X) + A_3 \exp(pX) + A_4 \exp(-X) \qquad (4.9)$$

where $$p = \sqrt{1 + \frac{\beta}{\alpha^2 \nu}} \qquad (4.9a)$$

When $\beta = 0$, the solution is

$$\varphi_{NS} = A_5 \exp(X) + A_6 \exp(-X) + A_7 X \exp(X) + A_8 X \exp(-X) \qquad (4.10)$$

The disturbance is assumed to vanish at large distances from this interface. There is no slip and there is continuity of tangential stress at the interface, which, besides, is a streamline. These assumptions lead to the following boundary conditions:

(i), (ii) $\varphi_A = \varphi'_A = 0$; $X = \infty$

(iii), (iv) $\varphi_B = \varphi'_B = 0$; $X = -\infty$

(v), (vi) $\varphi_A = \varphi_B = 0$; $X = 0$

(vii) $\varphi'_A = \varphi'_B$; $X = 0$

(viii) $\tau_{XYB} - \tau_{XYA} = \frac{\partial \sigma_{YY}}{\partial y}$; $X = 0$

where τ is the shear stress and σ_{yy} is the y component of the longitudinal surface stress (dynamic interfacial tension).

The shear stress is guven by:

$$\tau_{xyA} = \mu_A \left(\frac{\partial u_A}{\partial y} + \frac{\partial v_A}{\partial x}\right) \qquad (4.11)$$

$$\tau_{xyB} = \mu_B \left(\frac{\partial u_B}{\partial y} + \frac{\partial v_B}{\partial x}\right) \qquad (4.12)$$

where μ is the dynamic viscosity. For the dynamic interfacial tension the Boussinesq formulation is adopted which postulates that the departure of the tension from its steady-state value depends on the rate of deformation of the interface:

$$\sigma_{yy} = \sigma_o + \mu_S\,(\partial v/\partial y) \qquad (4.13)$$

where μ_S is the composite surface viscosity, and σ_o is the equilibrium interfacial tension. Deriving equation (4.13) with respect to y, a suitable expression for the right-hand side of boundary condition (viii) is obtained):

$$\frac{\partial \sigma_{yy}}{\partial y} = \frac{\partial \sigma_o}{\partial y} + \mu_S\,(\partial^2 v/\partial y^2) \qquad (4.14)$$

Since it is assumed in the model that the equilibrium concentration is reached instantaneously when changes in temperature are produced and since temperature and concentration are dependent variables in binary systems, the interfacial tension may be considered as a function of temperature only. As the temperature variations along the interface are assumed to be small it may be written that:

$$\frac{\partial \sigma_o}{\partial y} = \frac{d\sigma_o}{dT} \frac{\partial T}{\partial y} = \sigma_T \frac{\partial T}{\partial y} \qquad (4.15)$$

where $\sigma_T = d\sigma_o/dT$.

Combining equations (4.11), (4.12), (4.14) and (4.15) together with boundary condition (viii):

$$\sigma_T\left(\frac{\partial T}{\partial y}\right) + \mu_S\,(\partial^2 v/\partial y^2) = \mu_A\left(\frac{\partial u_A}{\partial y} + \frac{\partial v_A}{\partial x}\right) + \mu_B\left(\frac{\partial u_B}{\partial y} + \frac{\partial v_B}{\partial x}\right); \quad X = 0 \qquad (4.16)$$

Use of boundary conditions (i) to (vi) gives for $\beta \neq 0$

$$\varphi_A = A_2\,(\exp(-X) - \exp(-p_A X)) \quad ; \quad X \geq 0 \qquad (4.17)$$

$$\varphi_B = -A_2\,(1 - p_A)/(1-p_B)(\exp X - \exp(p_B X)) \quad ; \quad X \leq 0 \qquad (4.18)$$

The substitution of equations (4.6) and (4.17) into equation (4.16) gives, for $\beta \neq 0$:

$$\sigma_T\left(\frac{\partial T}{\partial y}\right)_{x=0} = A_2\alpha^2\mu_A\,(p_A - 1)\exp(i\alpha y)\exp(\beta t) \cdot \left(\frac{\mu_B}{\mu_A}(1 + p_B) + (1 + p_A) + \alpha\mu_S/\mu_A\right) \qquad (4.19)$$

Similarly, for $\beta = 0$

$$\varphi_{NSA} = A_8\ X \exp(-X) \qquad ; \quad X \geq 0 \qquad (4.20)$$

$$\varphi_{NSB} = A_8\ X \exp X \qquad ; \quad X \leq 0 \qquad (4.21)$$

$$\sigma_T \left(\frac{\partial T}{\partial y}\right)_{X=0} = 2\ A_8\ \alpha^2_{NS}/\mu_A \exp(i\alpha_{NS}\ y)\ (1 + (\mu_B/\mu_A) + /_{S}\alpha_{NS}/(2\mu_A)) \qquad (4.22)$$

To find out the temperature distribution along the interface, here assumed unidimensional, it is necessary to solve the perturbed equations of diffusion.

4.5 Equations of diffusion

The equations of heat and mass diffusion for the steady state are:

$$\begin{aligned} T^o_A &= T^o_I + \varepsilon_A\ x \qquad ; \qquad x > 0 \\ T^o_B &= T^o_I + \varepsilon_B\ x \qquad ; \qquad x < 0 \end{aligned} \qquad (4.23)$$

$$\begin{aligned} C^o_A &= C^*_A + \pounds_A\ x \qquad ; \qquad x > 0 \\ C^o_B &= C^*_B + \pounds_B\ x \qquad ; \qquad x < 0 \end{aligned} \qquad (4.24)$$

where $\varepsilon = \frac{dt}{dx}$,

$\pounds = \frac{dC}{dx}$,

T^o_I: temperature at the interface

and T^o and C^o denote the undisturbed temperature and concentration. The temperature and solute concentration are assumed to have been perturbed by the amounts $T^{\nabla}(x,u,t)$ and $C^{\nabla}(x,y,t)$ respectively, so that their instantaneous value is

$$T = T^{o} + T^{\nabla}(x,y,t)$$
$$C = C^{o} + C^{\nabla}(x,y,t) \qquad (4.25)$$

The perturbed temperature profiles are described by the two dimensional energy equation:

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = K \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) \qquad (4.26)$$

and the perturbed concentration profile by the two-dimensional diffusion equation:

$$\frac{\partial C}{\partial t} + \frac{\partial C}{\partial x} + \sigma \frac{\partial C}{\partial y} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) \qquad (4.27)$$

Inserting expressions (4.25) into equations (4.26) and (4.27) and neglecting terms of second order of smallness, the following equations are obtained:

$$\frac{\partial T^{\nabla}}{\partial t} + K \left(\frac{\partial^2 T^{\nabla}}{\partial x^2} + \frac{\partial^2 T^{\nabla}}{\partial y^2}\right) = - u \frac{dT^{o}}{dx} \qquad (4.28)$$

$$\frac{\partial C^{\nabla}}{\partial t} + D \left(\frac{\partial^2 C^{\nabla}}{\partial x^2} + \frac{\partial^2 T^{\nabla}}{\partial y^2}\right) = - u \frac{dC^{o}}{dx} \qquad (4.29)$$

Since the velocity, the temperature, and concentration perturbations must be of the same nature

$$T^{\nabla} = P(x) \exp(i\alpha y) \exp(\beta t) \qquad (4.30)$$

$$C^{\nabla} = H(x) \exp(i\alpha y) \exp(\beta t) \qquad (4.31)$$

Inserting these two equations into equations (4.28) and (4.29):

$$P'' - \left(1 + \frac{\beta}{\alpha^2 K}\right) P = - \frac{i\varepsilon}{\alpha K} \varphi(x) \qquad (4.32)$$

$$H'' - \left(1 + \frac{\beta}{\alpha^2 D}\right) H = - \frac{i\varepsilon}{\alpha D} \varphi(x) \qquad (4.33)$$

Both the above equations are of the same form. Sternling and Scriven give the solution to the mass diffusion equation, and this also applies to the heat diffusion equation:

$$P = A_9 \exp(gX) + A_{10} \exp(-gX) - nJ \qquad (4.34)$$

$$H = A_{12} \exp(qX) + A_{12} \exp(-qX) - lI \qquad (4.35)$$

where:

$$q = \left(1 + \frac{\beta}{\alpha^2 D}\right)^{\frac{1}{2}} \qquad g = \left(1 + \frac{\beta}{\alpha^2 K}\right)^{\frac{1}{2}}$$

$$l = i\epsilon/(\alpha D) \qquad n = i\epsilon/(\alpha K)$$

$$I = \exp(qX) \int \exp(-2qX) \int \exp(qX)\ (dX)^2$$

$$J = \exp(gX) \int \exp(-2gX) \int \exp(gX)\ (dX)^2$$

Equations (4.34) and (4.35) for each phase are:

$$P_A = A_9 \exp(g_A X) + A_{10} \exp(-g_A X) - n_A J_A \qquad (4.37)$$

$$P_B = B_9 \exp(g_B X) + B_{10} \exp(-g_B X) - n_B J_B \qquad (4.38)$$

$$H_A = A_{11} \exp(q_A X) + A_{12} \exp(-q_A X) - l_A I_A \qquad (4.39)$$

$$H_B = B_{11} \exp(q_B X) + B_{12} \exp(-q_B X) \quad l_B I_B \qquad (4.40)$$

Eight boundary conditions are necessary to determine the eight constants in equations (4.37) to (4.40). The first four are obtained from the assumption that the temperature and concentration disturbances vanish at large distances from the interface. In combination with equations (3.30) and (3.31), this gives

(ix), (x) $\quad P_A = H_A = 0 \quad ; \quad x = \infty$

(xi), (xii) $\quad P_B = H_B = 0 \quad ; \quad x = -\infty$

The temperature of the two phases are assumed to be the same at the interface in both the undisturbed and the disturbed states. Therefore, the temperature disturbance at the interface is the same in both phases:

$$\text{(xiii)} \qquad \overset{\blacktriangledown}{T}_A\,(o,y,t) = \overset{\blacktriangledown}{T}_B\,(o,y,t) \quad ; \quad x = 0$$

According to the linear dependence of the equilibrium concentration on temperature assumed in the model, the concentration disturbances are:

$$\text{(xiv)} \qquad \overset{\blacktriangledown}{C}_A\,(o,y,t) = R_A \overset{\blacktriangledown}{T'}_A(o,y,t) \quad ; \quad x = 0$$

$$\text{(xv)} \qquad \overset{\blacktriangledown}{C}_B\,(o,y,t) = R_B \overset{\blacktriangledown}{T}_B\,(o,y,t) \quad ; \quad x = 0$$

where R is the constant defined by equation (3.16).

The remaining boundary condition is the equation of conservation of energy at the interface, discussed in detail with respect to boundary condition (xii) in chapter 5,:

$$\text{(xvi)} \qquad - D_A \frac{\partial \overset{\blacktriangledown}{C}_A}{\partial x} Q^o_A + D_B \frac{\partial \overset{\blacktriangledown}{C}_B}{\partial x} Q^o_B = - k_A \frac{\partial \overset{\blacktriangledown}{T}_A}{\partial x} + k_B \frac{\partial \overset{\blacktriangledown}{T}_B}{\partial x} \; ; \; x = 0$$

Conditions (ix) to (xii) lead to:

$$A_9 = A_{11} = B_{10} = B_{12} = 0 \qquad (4.41)$$

From equation (4.41), equations (4.37) and (4.38) become:

$$P_A = A_{10} \exp(-g_A X) - n_A J_A \qquad (4.42)$$

$$P_B = B_9 \exp(g_B X) - n_B J_B \qquad (4.43)$$

Combining equation (4.30) and boundary condition (xiii):

$$P_A = P_B \; ; \quad x = 0 \qquad (4.44)$$

Inserting equations (4.42) and (4.43) into equation (4.44):

$$A_{10} = B_9 - n_B J_B + n_A J_A \quad ; \quad x = 0 \qquad (4.45)$$

From equations (4.30), (4.31), and (4.44) using boundary conditions (xiv) and (xv):

$$H_A = R_A P_A \quad ; \quad x = 0 \qquad (4.46)$$

$$H_B = R_B P_A \quad ; \quad x = 0 \qquad (4.47)$$

Constants A_{12} and B_{11} are obtained by inserting equation (4.41) into equations (4.39) and (4.40) and combining the resulting equations with equations (4.46) and (4.47):

$$A_{12} = R_A P_A - l_A I_A \quad ; \quad x = 0 \qquad (4.48)$$

$$B_{11} = R_B P_A - l_B I_B \quad ; \quad x = 0 \qquad (4.49)$$

On substituting equations (4.48) and (4.49) into equations (4.39) and (4.40) the solution for the x-components of the concentration disturbance in phases A and B are obtained:

$$H_A = (R_A P_A(o) - l_A I_A(o)) \exp(-q_A X) - l_A I_A(o) ; \quad x \geqslant 0 \qquad (4.50)$$

$$H_B = (R_B P_B(o) - l_B I_B(o)) \exp(q_B X) - l_B I_B(o) , \quad x \leqslant 0 \qquad (4.51)$$

It only remains to determine the constants A_{10} and B_9 to obtain the four solutions to the perturbed diffusion equations. Equation (4.45) relates the two constants, a second equation is obtained from boundary condition (xvi). On combining equations (4.30) and (4.31), with equations (4.42), (4.43), (4.43), (4.50) and (4.51), the four derivatives in boundary condition (xvi) become:

$$\frac{\partial \overset{\nabla}{C}_A}{\partial x} = \exp(i\alpha y) \exp(\beta t) \frac{dH_A}{dx} = - q_A (R_A P_A(o) - l_A I_A(o) - l_A I'_A(o) \quad ; \quad x = 0 \qquad (4.52)$$

$$\frac{\partial \overset{\nabla}{C}_B}{\partial x} = \exp(i\alpha y) \exp(\beta t) \frac{dH_B}{dx} = q_B (R_B P_B(o) - l_B I_B(o) - l_B I'_B(o) \quad ; \quad x = 0 \qquad (4.53)$$

$$\frac{\partial T'_A}{\partial x} = \exp(i\alpha y)\exp(\beta t)\frac{dP_A}{dx} = -g_A A_{10} - n_A J'_A(o) \quad ; \; x = 0 \tag{4.54}$$

$$\frac{\partial T'_B}{\partial x} = \exp(i\alpha y)\exp(\beta t)\frac{dP_B}{dx} = g_B B_9 - n_B J'_B(o) \quad ; \; x = 0$$

On inserting the four above equations into boundary condition (xvi) and combining the resulting equation with equation (4.45), the following expression for constant B_9 is obtained:

$$B_9 = (Q_{AB}n_B J_B(0) - D_A Q^o_A I_{AA} - D_B Q^o_B I_{BB})/(Q_{AB} - k_A g_A - k_B g_B)$$
$$+ k_A(J_{AA} - g_A n_B J_B(o)) - k_B n_B J_B(o)/(Q_{AB} - k_A g_A - k_B g_B) \tag{4.55}$$

where

$$\begin{aligned} Q_{AB} &= D_A Q^o_A R_A g_A + D_B Q^o_B R_B q_B \\ I_{AA} &= l_A\ (q_A I_A(o) + I'_A(o)) \\ I_{BB} &= l_B\ (q_B I_B(o) + I'_B(o)) \\ J_{AA} &= n_A\ (g_A J_A(o) + J'_B(o)) \end{aligned} \tag{4.56}$$

The expression for A_{10} is obtained by introducing equation (4.55) into equation (4.45). The values of the integral I and its derivative with respect to x are given by Sternling and Scriven. Since integrals I and J are of the same form, the values of J, as well as the values of its derivative, may be taken from the table presented by these authors for I. This table is reproduced in table 4.1, with a change in notation. The integral, which can be either I or J, has been denoted INT. The constant a denotes either q or g. On inserting the values of the integrals I and J and their derivatives given in table 4.1 into equation (4.55)

TABLE 4.1

QUANTITIES APPEARING IN EQUATIONS (4.17) to (4.55)

	β	Phase A $x \geqslant 0$	Phase B $x \leqslant 0$
$\varphi(X)/A$	$\neq 0$	$\exp(-X) - \exp(-\rho_A X)$	$-\frac{1-\rho_A}{1-\rho_B}\exp(X) - \exp(\rho_B X)$
INT(X)/A	$\neq 0$	$-\frac{\exp(-X)}{a^2_A - 1} - \frac{\exp(-\rho_A X)}{a^2_A - \quad {}_A^2}$	$-\frac{1-\rho_A}{1-\rho_B}\,\frac{\exp(X)}{a^2_B - 1} - \frac{\exp(\rho_B X)}{a^2_B - \rho^2_B}$
INT(O)/A	$\neq 0$	$\frac{\rho_A^2 - 1}{(a_A^2 - 1)(a_A^2 - \rho_A^2)}$	$-\frac{(1 - {}_A)(\;{}^2_B - 1)}{(1 - \rho_B)(a^2_B - 1)(a^2_B - \rho_B^2}$

TABLE 4.1 (continuation)

INT (o)/A	$\neq 0$	$\frac{(1-\rho_A)(a_A^2+\rho_A)}{(a_A^2-1)(a_A^2-{}_A^2}$	$\frac{(1-\rho_A)\ (a_B^2+\rho_B)}{(a_B^2-1)(a_B^2-\rho_B^2)}$
φ(X)/A	= 0	X exp (-X)	X exp (X)
INT(X)/A	= 0	- X(X + 1) exp (-X)/4	X(X - 1) exp (-X)/4
INT(o)/A	= 0	0	0
INT′(o)/A	= 0	-1/4	-1/4

and combining the resulting expression with equations (4.36), (4.43) and (4.44):

for $\beta \neq 0$:

$$P_A(o) = \frac{i}{\alpha}(1 - p_A)\left[\frac{\dfrac{k_A\varepsilon_A}{K_A(g_A+1)(g_A+p_A)} - \dfrac{k_B\varepsilon_B}{K_B(g_B+1)(g_B+p_B)}}{D_A\Omega^{o}{}_A R_A q_A + D_B\Omega^{o}{}_B R_B q_B - k_A g_A - k_B g_B} - \frac{\dfrac{\Omega^{o}{}_A\ \varepsilon_A}{(g_A+1)(q_A+p_A)} + \dfrac{\Omega^{o}{}_B\ \varepsilon_B}{(q_B+1)(q_B+p_B)}}{D_A\Omega^{o}{}_A R_A q_A + D_B\Omega^{o}{}_B R_B q_B - k_A g_A - k_B g_B}\right] \tag{4.57}$$

for $\beta = 0$

$$P_A(o) = -\frac{i}{\alpha_{NS}}\ \frac{\rho_A C_{PA}\varepsilon_A - \rho_B C_{PB}\varepsilon_B - \Omega^{o}{}_A\ \varepsilon_A + \Omega^{o}{}_B\ \varepsilon_B}{D_A\Omega^{o}{}_A R_A + D_B\Omega^{o}{}_B R_B - k_A - k_B} \tag{4.58}$$

Equations (4.57) and (4.58) give the x-component of the temperature disturbance at the interface.

The aim of this analysis is to determine the temperature distribution along the interface in the disturbed state. On inserting equation (4.30) into equation (4.25), the derivative of the perturbed temperature with respect to y at the interface is:

$$\frac{\partial T_A}{\partial y} = i\alpha P_A(o)\ \exp\ (i\alpha y)\ \exp\ (\beta t); \quad x = 0 \tag{4.59}$$

Since the temperature at the interface is the same for both phases, $\partial T_A/\partial y$ is equal to $\partial T_B/\partial y$.

Inserting equation (4.57), and (4.58), into equation (4.59):

for $\beta \neq 0$:

$$\frac{\partial T}{\partial y} = -(1-p_A)\ \frac{\rho_A C_{PA}\varepsilon_A/g_{AA}) - (\rho_B C_{PB}\varepsilon_B/g_{BB}) -}{Z_1}$$

$$-\ \frac{(\Omega^{o}{}_{A}\varepsilon_A/q_{AA}) + (\Omega^{o}{}_{B}\varepsilon_B/q_{BB})}{Z_1} \quad ; \quad x = 0 \qquad (4.60)$$

for $\beta = 0$:

$$\frac{\partial T}{\partial y} = \frac{\rho_A C_{PA}\varepsilon_A - \rho_B C_{PB}\varepsilon_B - \Omega^{o}{}_{A}\varepsilon_A + \Omega^{o}{}_{B}\varepsilon_B}{4\ (D_A\ \Omega^{o}{}_{A}\ R_A + D_B\ \Omega^{o}{}_{B}\ R_B - k_A - k_B\ )} \quad ; x = 0 \qquad (4.61)$$

where

$$g_{AA} = (g_A + 1)\ (g_A + p_A) \qquad g_{BB} = (g_B + 1)\ (g_B + p_B)$$

$$(4.61a)$$

$$q_{AA} = (q_A + 1)\ (q_A + p_A) \qquad g_{BB} = (q_B + 1)\ (q_B + p_B)$$

$$Z_1 = D_A\ \Omega^{o}{}_{A}\ R_A q_A + D_B\ \Omega^{o}{}_{B}\ R_B q_B - k_A g_A - k_B g_B \qquad (4.61b)$$

Equation (4.60) and (4.61) represent the desired temperature gradient at the interface.

4.6 Characteristic Equation

Inserting equations (4.60) and (4.61) into equations (4.19) and (4.22), and rearranging into dimensionless form, the characteristic equation is obtained:

for $\beta \neq 0$

$$M = \frac{(1/g_{AA}) - (1/sm\ g_{BB})}{Z_2\ Z_3} -$$

$$\frac{(\varepsilon_A/q_{AA}) - \varepsilon_B/\Omega^{o}{}_{C}\ q_{BB}) \quad E_A/\varepsilon_A}{Z_2\ Z_3} \qquad (4.62)$$

for $\beta = 0$

$$M_{NS} = \frac{1 - (1/sm) - (\mathcal{E}_A - \mathcal{E}_B\, \Omega^o{}_C)\, E_A/\, \varepsilon_A}{8\, Z_{20}\, Z_{30}} \qquad (4.63)$$

where:

$Z_2 = N_A\, q_A + N_B\, q_B - g_A - g_B/h^2m$

$Z_{20} = N_A + N_B - 1 - 1/h^2m$

$Z_3 = 1 + p_A + (1 + p_B)\ (\mu_B/\mu_A) + \alpha\mu_S/\mu_A$

$Z_{30} = 1 + (\mu_B/\mu_A) + \alpha_{NS}\ \mu_S/2\mu_A$

$$M = \frac{\mu_A K_A}{\sigma_T \varepsilon_A}\ \alpha^2 \qquad (4.63a)$$

$$N_A = E_A R_A/L_A \qquad (4.63b)$$

$$N_B = E_B R_B/\Omega^o{}_C r^2 L_A\ ;\quad s = \mathcal{E}_A/\mathcal{E}_B\ ;\quad \Omega^o{}_C = \Omega^o{}_A/\Omega^o{}_B \qquad (4.63c,d,e)$$

E_A, m, h^2 and r^2 are as defined in chapter 3. The temperature and concentration profiles in equations (4.62) and (4.63) are linked by the energy balance at the interface:

$$- D_A \mathcal{E}_A \Omega^o{}_A + D_B \mathcal{E}_B \Omega^o{}_B = - k_A \varepsilon_A + k_B \varepsilon_B \qquad (4.64)$$

Combining this equation with the terms containing the concentration profiles in equation (4.63), the following expressions are obtained for mass transfer taking place in one phase only:

$$- E_A \mathcal{E}_A/\varepsilon_A = - L_A(1 - 1/h^2 sm) \quad ; \quad \text{phase B saturated} \quad (4.65$$

$$E_A \mathcal{E}_B/\varepsilon_A \Omega^o{}_C = - L_A\ r^2\ (1 - 1/h^2 sm) ; \text{phase A saturated} \quad (4.66$$

Introducing equations (4.65) and (4.66) into equations (4.62) and (4.63):

for $\beta \neq 0$

$$M = \frac{(1/g_{AA}) - (1/sm\ g_{BB})}{Z_2\ Z_3} - L_A\ \bar{n}\ \frac{(1/q_{AA}) - 1/h^2 sm\ q_{BB}}{Z_2\ Z_3} \qquad (4.67)$$

where $\bar{n} = 1$ for phase B saturated

$\bar{n} = r^2$ for phase A saturated (4.68)

for $\beta = 0$

$$M_{NS} = \frac{1 - (1/sm - L_A \bar{n}\ (1 - 1/h^2 sm)}{8\ Z_{20}\ Z_{30}} \qquad (4.69)$$

The dimensionless groups as defined by equation (4.63a) is the inverse of the Marangoni number with the characteristic linear dimension represented by $1/\alpha$. As the characteristic equation has been developed for semi-infinite media, there is no other length scale to which this number could be referred to. The Marangoni number may be interpreted as the ratio of the destabilising surface tension forces to the stabilising viscous forces.

From equations (3.11), (3.16), (3.35), and (4.63b, c, e), the dimensionless numbers N_A and N_B may be written as:

$$N_A + N_B = \frac{\Omega^o{}_A\ D_A\ C^\nabla{}_A + \Omega^o{}_B\ D_B\ C^\nabla{}_B}{\rho_A\ C_{PA}\ K_A\ T^\nabla} \qquad (4.70)$$

Physically, this group represents the ratio of the change in the rate of heat production with temperature to the heat flux in phase A associated with the temperature perturbation.

Equations (4.62) and (4.63) establish the relation between the wave length of the disturbance and the amplification factor. Unfortunately equation (4.62) is implicit and a trial and error technique is necessary to find out the pair of values of α and β for a given system. A detailed study of the behaviour of equation (4.62) under diverse physical conditions will lead to the understanding of the rôle played by the physical parameters in the stability problem.

Since the amplification factor β always appears divided by α^2 in the equation (4.62), it is convenient to define a new variable:

$$\gamma = \frac{\beta}{\alpha^2 K_A} \qquad (4.71)$$

Combining the dimensionless wave number, M, with α another dimensionless group G is defined:

$$G = \gamma . M = \mu_A \beta / (\sigma_T \varepsilon_A) \qquad (4.72)$$

The group G may be regarded as the dimensionless growth constant. In terms of the new variable γ the groups P, q and g, defined by equations (49a) and (4.36) respectively, become:

$$\begin{aligned} g_A &= \sqrt{1 + \gamma} & g_B &= \sqrt{1 + h^2 \gamma} \\ p_A &= \sqrt{1 + j^2 \gamma} & p_B &= \sqrt{1 + e^2 j^2 \gamma} \\ q_A &= \sqrt{1 + L_A \gamma} & q_B &= \sqrt{1 + r^2 L_A \gamma} \end{aligned} \qquad (4.73)$$

where: $h^2 = K_A / K_B$ $e^2 = \nu_A/\nu_B$

$i/j^2 = \nu_A / K_A$ Prandtl number $r^2 = D_A/D_B$

The four terms defined by expressions (4.61a) combined with equations (4.73) are:

$$
\begin{aligned}
(g_A + 1)^{-1} (g_A+p_A)^{-1} &= (g_A-1) \;/\; (g_A + p_A)\gamma \\
(g_B+ 1)^{-1} (g_B+p_B)^{-1} &= (g_B-1) \;/\; (g_B+p_B)\, h^2\gamma \\
(q_A+ 1)^{-1} (q_A+p_A)^{-1} &= (q_A-1) \;/\; (q_A+p_A)\, L_A\gamma \\
(q_B+ 1)^{-1} (q_B+p_B)^{-1} &= (q_B-1) \;/\; (q_B+p_B)\, r^2 L_A\gamma
\end{aligned}
\qquad (4.74)
$$

Inserting equations (4.75) into equation (4.62) and combining with equation (4.73), the following expressions for G are obtained:

for mass transfer in both directions:

$$
G = \frac{(g_A - 1)/(g_A+p_A) - (g_B-1) / smh^2 (g_B + p_B)}{Z_2\ Z_3} - \frac{\left[\varepsilon_A (q_A-1) / (q_A+p_A) - \varepsilon_B (q_B-1) / r^2\, \Omega^{o}{}_{C} (q_A+p_A)\right] E_A/L_A\varepsilon_A}{Z_2\ Z_3} \qquad (4.75)
$$

for mass transfer in one direction only:

$$
G = \frac{(g_A - 1) / (g_A+p_A) - (g_B - 1) / smh^2 (g_B + p_B)}{Z_2\ Z_3} - \frac{L_A\bar{n} (1 - 1/h^2 ms) (q_k - 1) / (q_k+ p_k) (q_k + 1)}{Z_2\ Z_3} \qquad (4.76)
$$

where subscript $k = A$ for phase B saturated

$k = B$ for phase A saturated.

Equation (4.63) is the limit of equation (4.62) for $\beta = 0$, that is for $\gamma = 0$. A study of equations (4.62) and (4.75) in the vicinity of the point $\gamma = 0$ and for large values of γ will give information about the behaviour of binary systems with respect to stationary and oscillatory instabilities.

4.7 Limiting behaviour of the characteristic equation

The development of the expansions of equation (4.62) for small and large values of γ leading to the equations presented in this section are presented in Appendix A.

4.7.1. Small values of γ

For $\gamma \to 0$ equation 4.62 becomes:

$$M = \frac{1 - (1/sm) - (\mathcal{E}_A - \mathcal{E}_B/\Omega^{o}_{C})\, E_A/\varepsilon_A}{8\, Z_{20}\, Z_{30}} \cdot (1 - f\gamma) \qquad (4.77)$$

where:

$$f = \frac{1 - (h^2/sm) - (\mathcal{E}_A - \mathcal{E}_B r^2/\Omega^{o}_{C})\, L_A E_A}{Z_4\, \varepsilon_A} +$$

$$+ \frac{j^2 \left[1 - (e^2/sm) - (\mathcal{E}_A - \mathcal{E}_B e^2/\Omega^{o}_{C})\right] E_A}{4\, Z_4\, \varepsilon_A} +$$

$$+ \frac{E_A\, (R_A + R_B / \Omega^{o}_{C}) - 1 - 1/m}{2\, Z_{20}} +$$

$$+ \frac{1 + (e^2 \mu_B/\mu_A)\ j^2}{4\ Z_{30}} \qquad (4.78)$$

where:

$$Z_4 = 1 - (1/sm) - (\mathcal{E}_A - \mathcal{E}_B/\Omega^{o}{}_{C})\ E_A/\varepsilon_A \qquad (4.78a)$$

The first factor in equation (4.77) is, according to equation (4.63), the dimensionless wave number for $\beta = 0$. This is the wave number corresponding to the neutral stability regime and is denoted by M_{NS}. Thus, equation (4.77) may be written as:

$$M = M_{Ns}\ (1 - f\gamma) \quad ; \quad \text{for} \quad \gamma \to 0 \qquad (4.79)$$

Equation (4.79) may be interpreted as the first two terms of an expansion of the function $M(\gamma)$ in a Maclaurin series. Then the factor $-f$ may be regarded as the derivative of $M(\gamma)$ with respect to γ at the point $\gamma = 0$. When mass transfer takes place in only one direction the corresponding expression for M_{Ns} is given by equation (4.69). Combining equation (4.78) with equations (4.65) and (4.66), the expression for f for unidirectional mass transfer becomes:

$$f = \frac{1 - (h^2/sm) - L_A\bar{n}\ (1 - 1/h^2 sm)}{Z_5} +$$

$$+ \frac{j^2\ (1 - e^2/sm) - L_A b\ (1 - 1/h^2 ms)}{4\ Z_5}$$

$$+ \frac{E_A\ (R_A + R_B/\Omega^{o}{}_{C}) - 1 - 1/m}{2\ Z_{20}} +$$

$$+ \frac{(1 + e^2\mu_B/\mu_A)\ j^2}{4\ Z_{30}} \qquad (4.80)$$

where $\bar{n} = 1$ and $b = 1$, for phase B saturated

$\bar{n} = r^2$ and $b = r^2 e^2$, for phase A saturated

$$Z_5 = 1 - (1/sm) - L_A n\ (1 - 1/h^2 sm)$$

Inserting equation (4.79) into equation (4.72), the dimensionless growth constant becomes, for small values of γ:

$$G = M_{NS}\ (\gamma - f\ \gamma^2) \tag{4.81}$$

4.7.2. Large values of γ

For $\gamma \to \infty$, equation (4.62) becomes:

$$\begin{aligned} M = & \left[\frac{1/(1+j) - 1/smh\ (h+je)}{Z_6\ Z_7\ j\ \sqrt{L_A}\ \varepsilon_A} \right. \\ & - \left. \frac{\mathcal{E}_A/(j + \sqrt{L_A} - \mathcal{E}_B/\Omega^o{}_C\ r\ (je + r\sqrt{L_A})}{Z_6\ Z_7\ j\ \sqrt{L_A}\ \varepsilon_A} \right] \gamma^{-2} \\ & + \left\{ \frac{\left[(je+1)/(j+1) - (1/smh^2)\right] \mu_B}{Z_6\ Z^2{}_7\ j^2 \mu_A} \right. \\ & - \frac{\left[\mathcal{E}_A\ (je + \sqrt{L_A})/(j + \sqrt{L_A}) - \mathcal{E}_B/\Omega^o{}_C r\right] \mu_B}{Z_6\ Z^2{}_7\ j^2 \mu_A L_A \varepsilon_A} \\ & + \frac{1 - \left[(h+j)/smh^2(h+je)\right] - E_A(\mathcal{E}_A - \mathcal{E}_B/\Omega^o{}_C r^2)\, \varepsilon_A L_A}{Z_6\ Z^2{}_7\ j^2} \\ & + \frac{1/(1+j) - 1/smh(h+ej)}{Z_6\ Z^2{}_7\ j^2 \mu_A} \alpha \mu_S \\ & - \left. \frac{\mathcal{E}_A/(j+\sqrt{L_A}) - \mathcal{E}_B/\Omega^o{}_B r\ (je + r\sqrt{L_A})}{Z_6\ Z^2{}_7\ j^2\ \varepsilon_A\ \sqrt{L_A}/\mu_A}\ E_A\ \alpha\mu_S \right\} \gamma^{-5/2} \end{aligned} \tag{4.82}$$

where:

$$Z_{60} = (R_A + R_B/\Omega_C^{o} r_-)\ E_A/L_A - 1 - 1/hm \qquad (4.82a)$$

$$Z_{70} = (e\ \mu_B/\mu_A) + 1 \qquad (4.82b)$$

Combining equations (4.65) and (4.66) with equation (4.82), the expressions for unidirectional mass transfer are obtained:

$$M = \frac{(e\sqrt{L_A} - h)\ (1 + j) - smh^2\ (\sqrt{L_A} - 1)\ (h + je)}{Z_6\ Z_7\ Z_8\ (h + je)}\ \gamma^{-2}$$
$$+ \left\{ \frac{\left[smh^2\ (\sqrt{L_A} - 1) + j + 1\right] \mu_B/\mu_A + 1}{Z_6\ Z_7^2\ Z_8\ (e + 1)\ j}\ (e^2 - 1) \right.$$
$$\left. + \frac{(e\sqrt{L_A} - h)(1 + j) - smh^2\ (\sqrt{L_A} - 1)\ (h + je)}{Z_6\ Z_7^2\ Z_8\ j\mu_A}\ \alpha\mu_S \right]\ \gamma^{-5/2} \qquad (4.83)$$

for phase B saturated

where $Z_8 = (1 + j)\ (j + \sqrt{L_A})\ h^2 sm$ (4.83a)

and

$$M = \frac{(r\sqrt{L_A} - h)\ (1 + j) - smh^2\ (r\sqrt{L_A} - e)\ (h + je)}{Z_6\ Z_7\ Z_9\ (je + r\sqrt{L_A})}\ \gamma^{-2}$$
$$+ \frac{smh^2\ (h + je)\mu_B/\mu_A + j + 1}{Z_6\ Z_7^2\ Z_9\ (e + 1)\ j}\ (e^2 - 1)$$
$$+ \frac{(r\sqrt{L_A} - h)\ (1 + j) - smh^2\ (r\sqrt{L_A} - e)\ (h + je)}{Z_6\ Z_7^2\ Z_9\ j\mu_A}\ \alpha\mu_S\ \alpha^{-5/2}$$

for phase A saturated,

where $Z_9 = (1 + j)\ (h + je)$ (4.84a)

Equations (4.82) to (4.84) have the form:

$$M = a\,\gamma^{-2} + b\,\gamma^{-5/2} \tag{4.85}$$

Combining this equation with equation (4.72), the corresponding expression for B is:

$$B = a_M\gamma^{-1} + b_M\gamma^{-3/2} \tag{4.86}$$

4.8 Analysis of the characteristic equation

When the values of the physical properties of a given system are inserted into equation (4.75), equation (4.72) determines the complex growth constant β for each wave number α. Apart from α and β, which have been defined in equations (4.6a) and (4.6b) respectively, it is interesting to introduce their ratio:

$$c = \beta/\alpha = c_r + ic_i$$

Here c_r determines the velocity of damping or amplification of the disturbance and c_i denotes the velocity of propagation of the wave in the y direction. Table 4.2 shows possible combinations of values of β_r and β_i. When $\beta_r < 0$ and $\beta_r \leqslant 0$, the amplitude and velocity of propagation of the disturbances decay with time. Hence, case 1 describes a stable system.

Table 4.2

Case	β_r	β_i	c_r	c_i	Observations
1	<0	$\leqslant 0$	<0	$\leqslant 0$	Stable system.
2	>0	$=0$	>0	$=0$	Disturbances grow in place.
3	$=0$	$=0$	$=0$	$=0$	Neutral stability regime.
4	$=0$	>0	$=0$	>0	Neutral oscillatory regime.
5	>0	>0	>0	>0	Disturbances grow and translate.

In cases 2 and 3 the velocity of propagation is equal to zero. Therefore, the disturbance remains in place and the resulting regime of instability is called stationary or convective. Cases 4 and 5, in which the disturbance displays a propagation velocity $c_i > 0$, represent the oscillatory regime. In both regimes, the case $\beta_r = 0$, wherein the disturbance neither grows nor decays, corresponds to the minimum wave length for which the system is unstable. Therefore, the study of cases 3 and 4 is of special interest because they mark the boundary between the stable and the unstable state for a given system.

Equation (4.72) may be written as:

$$(M_r + iM_i)\ (\gamma_i^2 + \gamma_r^2) = G_r\gamma_r - G_i\gamma_i + (G_i\gamma_r - G_r\gamma_i)\ i \qquad (4.87)$$

Since M is the dimensionless wave number, and this is a real parameter, the component M_i must be equal to zero. This condition requires the imaginary component of the right hand side of equation (4.87) to be equal to zero, that is:

$$G_i\gamma_r - G_r\gamma_i = 0 \qquad (4.88)$$

The three solutions of equation (4.88) are:

(a) for $\gamma_r \neq 0$:

$$\gamma_i = 0 \quad \text{(and consequently } G_i = 0\text{)} \qquad (4.89)$$

(b) for $\gamma_i \neq 0$:

$$\gamma_r = G_r = 0 \qquad (4.90)$$

(c) for $\gamma_i \neq 0$ and $\gamma_r \neq 0$

$$G_i\gamma_r = G_r\gamma_i \qquad (4.91)$$

Solution (a) corresponds to the stationary regime, case 2, and solution (b) to the neutral oscillatory regime, case 4.

4.8.1. Case (a): $\gamma_r \neq 0$, $\gamma_i = 0$. Stationary regime

The neutral stability regime ($\beta_r=0$, $\beta_i=0$) represented by equation (4.63) is a special case of the stationary regime. As stated before, the wave number of neutral stability represents the minimum wave length for which a system shows stationary instability. Disturbances of larger wave length will grow with time, that is $\gamma_r=0$ for $\alpha<\alpha_{NS}$. Hence, equation (4.63) establishes the conditions for the onset of stationary instability and its analysis will lead to the stability criteria with respect to the stationary regime.

Since the wave number must be real, and M_{NS} contains α^2_{NS}, the right-hand side of equation (4.63) must have the same sign as M_{NS}. According to equation (4.63a) the sign of M depends on the signs of σ_T and ε_A. On the right-hand side of equation (4.63), the values of the rate of change of equilibrium concentration with temperature, R_A and R_B, vary from 0.01 to 0.1 g mol/^{o}C, the Lewis number is around 100, and the values of E_A range between 1 and 10 ^{o}C 1/g mol, these values being typical for most binary liquid systems. Therefore, the values of the dimensionless groups N_A and N_B are smaller than one and the denominator of equation (4.63) is negative. The equation for unidirectional mass transfer - equation (4.68) - is more suitable than equation (4.63) to analyse the sign of the numerator because it does not contain the concentration profiles. Since s, the ratio of the temperature profiles, is always negative, and all the other parameters are positive, the two terms in the numerator of equation (4.68) containing s are positive. Since r^2 and h^2 range between 0.5 and 5 for most pairs of liquids, the negative term containing L_A will be much larger than the addition of the two positive terms and the numerator will be negative. Consequently, the right-hand side of equation (4.63) is positive for any direction of transfer. Therefore, for stationary instability to be possible, M must be positive. If M is negative, the system is stable with respect to stationary instabilities.

The dimensionless wave number is positive when σ_T and ε_A have the same sign and negative when their signs are opposite. If the heat of solution of the liquid A in B has the same sign as the heat of solutions of B in A, the sign of ε_A does not depend on the direction of transfer. In such a case, depending on the sign of σ_T, the system will be either stable or unstable with respect to stationary instabilities in both directions of transfer.

Table 4.3A, B, and C contain the factors which define the signs of M_r, M_i and G_r in equations (4.79) and (4.81) in their unidirectional transfer form, and equations (4.83), (4.84) and (4.85). In the table, according to the previous discussion, the sign of Z_{20} defined by equation (4.82a) is negative and the ratio s is presented in terms of its absolute value: $s \doteq - |s|$. In addition, to simplify the forthcoming analysis, the term containing μ_S has been neglected. This is equivalent to assuming that the surface deformation term in the Boussinesq approximation, equation (4.13), is small compared with

TABLE 4.3

LIMITING BEHAVIOUR OF EQUATIONS (4.67) and (4.76)*

Part A: M_r

γ_r	γ_i	Direction of transfer	M_r
$\to 0$	$=0$	B→A	$-1 + (1/\lvert s\rvert m) - L_A\bar{n}(1 + 1/h^2\lvert s\rvert m)$
		A→B	
$=0$	$\to 0$	B→A	
		A→B	
$=0$	$\to\infty$	B→A	$-\left[1(e\sqrt{L_A} - h)(1 + j) + (\sqrt{L_A} - 1)(h + je)h^2\lvert s\rvert m\right]\gamma_i^{-2}$
		A→B	$-\left[(r\sqrt{L_A} - h)(1 + j) + (r\sqrt{L_A} - e)(h + je)h^2\lvert s\rvert m\right]\gamma_i^{-2}$
$\to\infty$	$\to 0$	B→A	$\left[(e\sqrt{L_A} - h)(1 + j) + (\sqrt{L_A} - 1)(h + je)h^2\lvert s\rvert m\right]\gamma_r^{-2}$
		A→B	$\left[(r\sqrt{L_A} - h)(1 + j) + (r\sqrt{L_A} - e)(h + je)h^2\lvert s\rvert m\right]\gamma_r^{-2}$

---

* Inherent positive factors are omitted.

TABLE 4.3 (continuation)

Part B: M_i

γ_r	γ_i	Direction of Transfer	M_i
→0	=0	B→A	0
		A→B	
=0	→0	B→A	$[1 + (1/|s|m) - L_A\bar{n}\ (1 + 1/h^2|s|m) \quad f\gamma_i$
		A→B	
=0	→∞	B→A	$\{1 + [j + 1 + h^2|s|m\ (1 - \sqrt{L_A})]\mu_B/\mu_A\}(e^2-1)\gamma_i^{-5/2}$
		A→B	$[j + 1 + h^2|s|m\ (h + je)\mu_B/\mu_A]\ (e^2 - 1)\ \gamma_i^{-5/2}$
→∞	=0	B→A	0
		A→B	

TABLE 4.3 (continuation)

Part C: G_r

γ_r	γ_i	Direction of transfer	G_r
→0	=0	B→A A→B	$\left[1 + (1/\lvert s\rvert m) - L_A\bar{n}\,(1 + 1/h^2\lvert s\rvert m\right]\gamma_r$
=0	→∞	B→A A→B	$-\left[1 + (1\lvert s\rvert m) - L_A\bar{n}\,(1 + 1/h^2\lvert s\rvert m)\right]f\gamma_i^{2}$
=0	→∞	B→A	$-\left\{1 + \left[j + 1 + \lvert s\rvert\,m\,h^2(1 - \sqrt{L_A})\right]\mu_B/\mu_A\right\}(e^2 - 1)\gamma_i^{-3/2}$
		A→B	$-\left[j + 1 + \lvert s\rvert\,m\,h^2\,(h + je)\mu_B/\mu_A\right](e^2 - 1)\gamma_i^{-3/2}$
→∞	=0	B→A	$\left[(e\sqrt{L_A} - h)\,(1 + j) + (r\sqrt{L_A} - e)\,(h + je)h^2\lvert s\rvert m\right]\gamma_r^{-1}$
		A→B	$\left[(r\sqrt{L_A} - h)\,(1 + j) + (r\sqrt{L_A} - e)\,(h + je\,h^2(s)m\right]\gamma_r^{-1}$

the change of interfacial tension with temperature. It must be noticed with respect to the values of M or G for $\gamma = 0$ that they may correspond either to $\beta = 0$ or $\alpha \to \infty$. The first possibility corresponds to α_{NS}. In both cases G, which is equal to γM, is equal to zero and the stationary disturbance does not grow with time. There may be other possibilities of $G = 0$ for $\gamma_r \neq 0$ when the numerator of equation (4.75) is equal to zero. It may be seen in table 4.3 (C) that the sign of G_r will, in general be positive for both $\gamma_i = 0$, $\gamma_r \to 0$ and $\gamma_i = 0, \gamma_r \to \infty$. Consequently, there may be none or an even number of eigenvalues of G_r. Since the parameters appearing in the numerator of equation (4.75) are numerous, an analytical determination of the conditions for $G = 0$ when $\gamma_r \neq 0$, is not possible.

4.8.2 Case (b): $\gamma_r = G_r = 0$

Since $\gamma_i \neq 0$, this case represents the neutral oscillatory regime. As before, the analysis will be carried out for mass transfer taking place in one direction only. From table 4.3(C), it can be seen that for the limit $\gamma_r = 0$, $\gamma_i \to 0$ the sign of G_r is positive in both directions of transfer, for the ranges of magnitude of the parameters $j = \sqrt{K_A/\mathcal{D}_A}$ is in general smaller than one. Since $L_A \gg 1$, in the limit $\gamma_r = 0, \gamma_i \to \infty$, G_r has the same sign as $(e^2 - 1)$ for transfer from phase B to phase A, and the sign of $(e^2 - 1)$ for the opposite direction of transfer. It may be concluded that if $e^2 < 1$ there is at least one value of γ_i for which $G_r = 0$. For mass transfer in the direction A → B, if $e^2 > 1$ there is at least one eigenvalue of G_r, but there may be an odd number of them. Therefore, binary systems are always unstable with respect to oscillatory instabilities when mass transfer takes place out of the phase of higher viscosity.

4.8.3 Case (C): $\gamma_r G_i = \gamma_i G_r$, $\gamma_i \neq 0$, $\gamma_r \neq 0$

This case represents the oscillatory regime and corresponds to case 5 in table 4.2. Since this is a general solution of equation (4.88), it is interesting to find out under what conditions cases (A) and (B) are particular solutions of this general case. The analysis of case (B) showed that there is always one unstable direction of transfer with respect to roll cells. Consequently, case (B) is a particular solution of case (C). For stationary instability to be possible, case (A), σ_t and ε_A must have the same sign. Therefore, stationary instability is not a particular solution of case (C), when the signs of σ_T and ε_A are not the same.

4.8.4 Summary

The conclusions of the stability analysis suggest a criteria of stability that can be summarised as follows:

(i) Stationary instabilities are promoted by positive heat of solution, i.e. negative temperature gradient in the upper phase, in systems with a negative change of interfacial tension with temperature and by negative heat of solution, i.e. positive temperature gradient in the upper phase, in systems with a positive change of interfacial tension with temperature.

(ii) Oscillatory instabilities are most likely to occur when mass transfer takes place out of the phase of higher viscosity.

(iii) Systems may be stable in both directions of transfer when the heat of solution and the change of interfacial tension with temperature are of the same sign, provided the ratio of viscosities is equal to one.

CHAPTER 5

STABILITY ANALYSIS OF SELECTED SYSTEMS

The equations developed in chapters 3 and 4 are applied in this chapter to the stability of six liquid pairs selected from the 46 systems investigated by Ying and Sawistowski$^{(16)}$.

Since binary systems exhibiting instabilities in one direction of transfer are also unstable when mass transfer takes place in both directions simultaneously, the stability analysis will be carried out for uni-directional mass transfer only.

In order to solve the characteristic equation for mass transfer in only one direction, equation (4.67), the temperature profiles were developed for unsteady conditions. They are, therefore, non-linear and the profiles obtained from equations (3.46) and (3.47) have to be linearised. In section 5.3 the concentration and temperature profiles for the selected systems at an initial temperature of 25 °C are computed and the temperature profiles are linearised using a standard technique.

The determination of and the literature sources for the values of the physical parameters appearing in equations (4.67), (3.46) and (3.47) are described in section 5.2.

The stability analysis of the six selected systems is reported in section 5.4.

5.1 Selection of systems

The systems selected were: ethyl acetate - water acetylacetone-water, isobutanol-water, methyl ethyl ketone water, cyclohexanol-water and hexane-aniline. The choice was made on the basis of the following considerations:

(i) The system should belong to different categories in Ying and Sawistowski's (16) classification of binary systems according to the intensity of the interfacial activity.

(ii) The liquid pairs should be representative of the following cases: unstable in one direction of transfer only, unstable in both directions of transfer and stable in both directions of transfer.

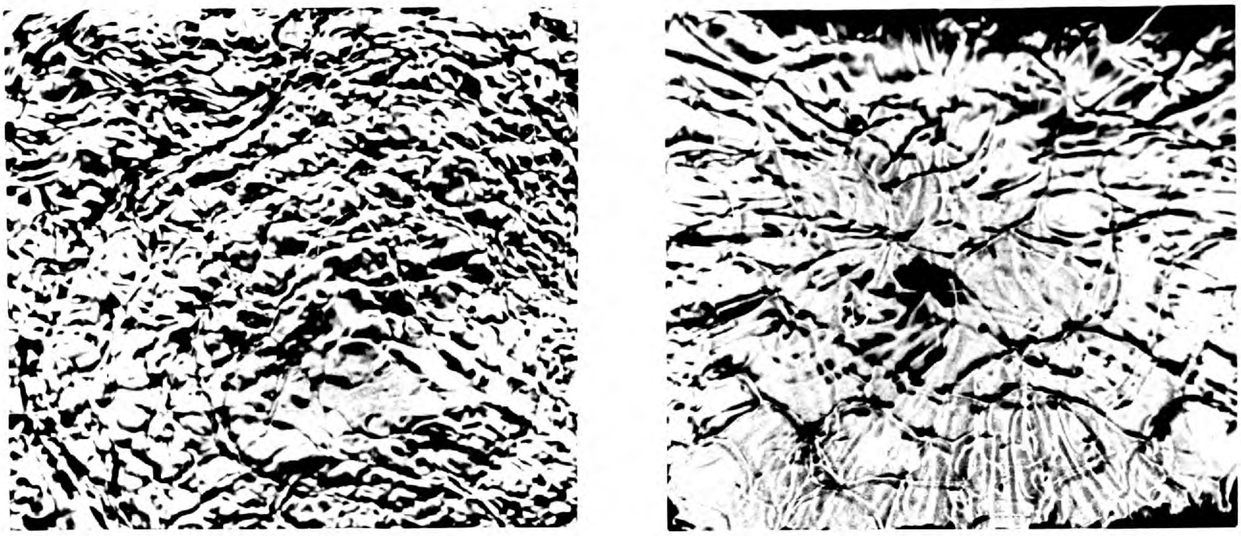
(iii) It is desirable for the systems to cover a wide range of values of the physical parameters.

Table 5.1 summarises the results obtained by Ying and Sawistowski on intensity of interfacial convection and directional effects for the selected systems. The results of the observations for simultaneous mass transfer in both directions are reported in decreasing order of intensity in the column labelled "Intensity of interfacial convection". The system acetylacetone-water shows instabilities of the most intense type when acetylacetone is transferred from the water saturated acetylacetone phase to pure water and is stable in the reverse direction. A schlieren photograph of the plane interface of this system after two minutes of contacting the phases is shown in figure 5.1(a) (9). The systems cyclohexanol-water and ethyl acetate-water belong to the same category,

TABLE 5.1

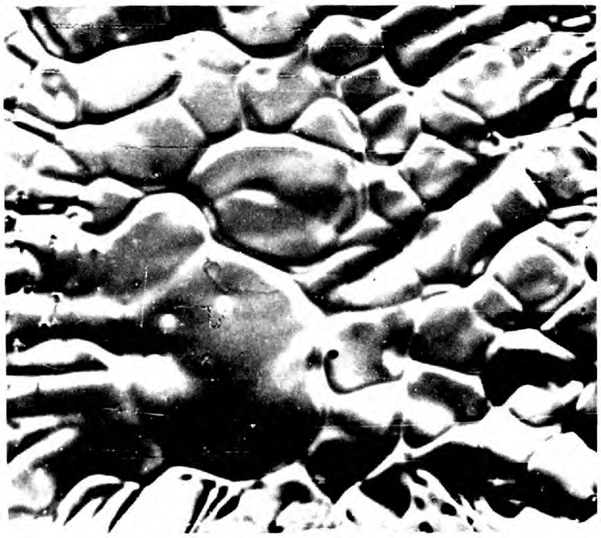
CLASSIFICATION OF THE SELECTED SYSTEMS (16)

Liquid A	Liquid B	Intensity of interfacial convection	Observations for direction of transfer	
			A → B	B → A
acetyl acetone	water	interfacial turbulence	turbulence	diffusional
cyclohexanol	water	convection cells	stationary cells	stationary cells
ethyl acetate	water	convection cells	streaks	drifting cells
hexane	aniline	streaks	streaks	streaks
isobutanol	water	diffusional	diffusional	diffusional
methyl ethyl ketone	water	diffusional	-	-



(a) Acetylacetone – Water

(b) Ethyl acetate – Water



(c) Cyclohexanol – Water

FIG. 5.1. UNSTABLE BINARY SYSTEMS

showing convection cells when mass transfer takes place in both directions simultaneously. For mass transfer in only one direction the system ethyl acetate-water is less active when ethyl acetate is transferred into water, while the cyclohexanol-water pair exhibit the same intensity in both directions. Figures 5.1(b) and (5.1(c)$^{(16)}$ show the interface of the systems ethyl acetate-water and cyclohexanol-water. Comparing the two interfaces the difference between roll cells and drifting cells can be realised immediately. The system isobutanol-water is stable in both directions of transfer and the pair methyl ethyl ketone-water was not investigated for directional effects.

5.2 Physical properties

The physical properties appearing in equations (3.44) to (3.47) and (4.67) were taken from experimental data reported in the literature. Whenever possible when data were not available they were either calculated with approximate equations or measured experimentally.

The heat capacity and the heat diffusivity of all the saturated solutions and the viscosity of the saturated solutions in the systems cyclohexanol-water and methyl ethyl ketone-water were estimated assuming a linear variation of their value with molar fraction. For example, the heat capacity of the saturated phase A was assumed to be:-

$$C^{*}_{pA} = x_A^{*} \, C_{pA} + (1 - x_A^{*}) \, C_{pB} \qquad (5.1)$$

where x_A^* = molar fraction of A at saturation.

C_{pA} and C_{pB} = heat capacity of the pure liquids A and B.

Table B1, appendix B contains values of parameters ρ, C_p, μ, ν and K for the pure liquids and tables B2 and B3 contain the same properties for the saturated solutions.

5.2.1 Density

All data for the pure liquids at 25 °C were taken from experimental data reported in the literature. For the saturated solutions density measurements were made using a 50 ml. standard specific gravity bottle. The weighings were performed using an automatic balance reading ± 0.0001 g. The densities of the saturated solutions were measured at 22, 25 and 28 °C. The data at 22 and 28 °C were needed for the calculation of interfacial tensions. The results for saturated liquids presented in figures 5.2 to 5.7 are the average of at least two determinations.

5.2.2 Heat capacity

The data for pure acetylacetone and cyclohexanol were not available in literature. They were calculated with the help of the additive contribution method of Johnson and Huang(39). The method predicts the heat capacity of organic liquids with 5 and 14 per cent average and maximum errors. The data for the saturated solutions were estimated using equation (5.1).

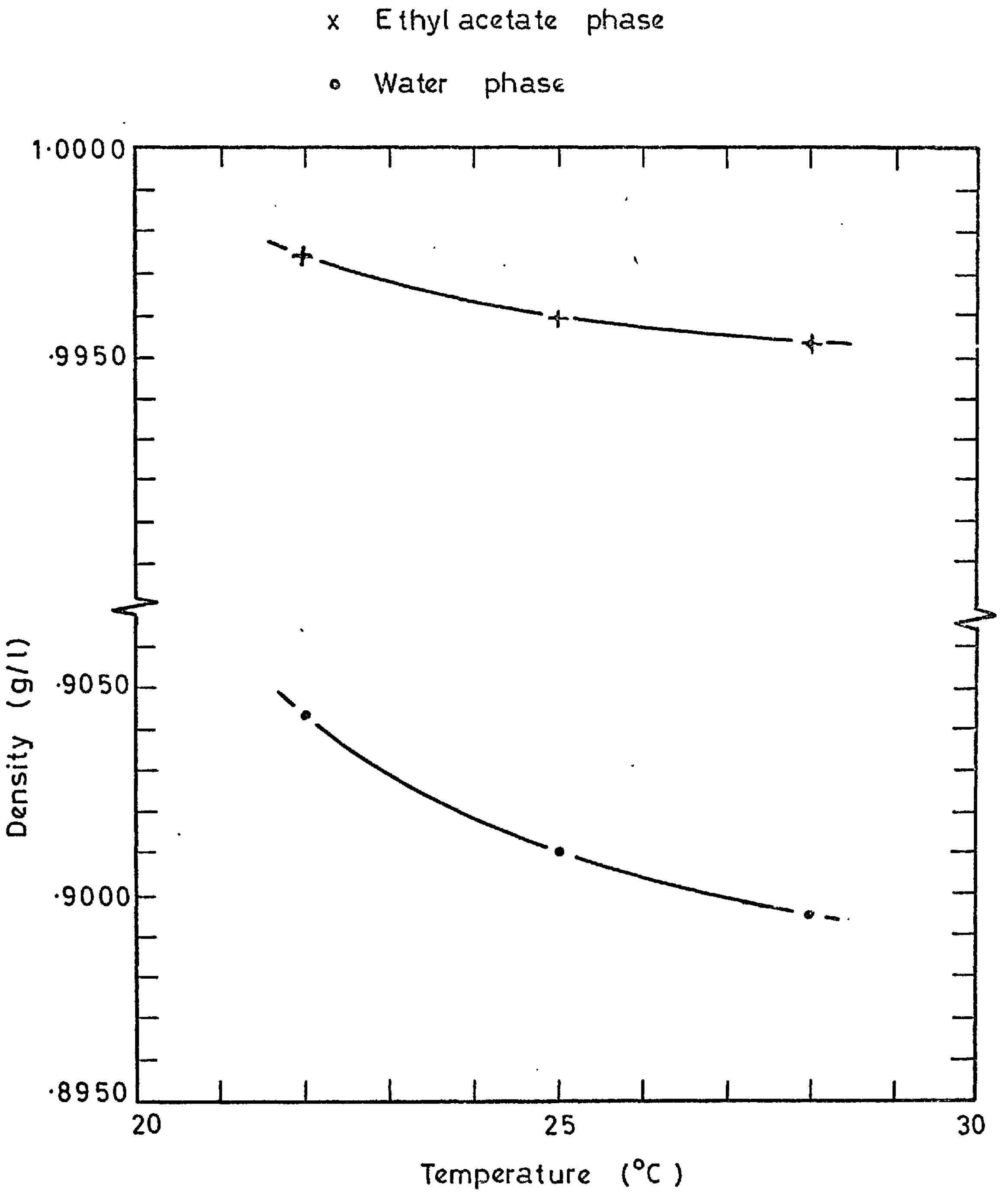


FIG. 5·2 DENSITY OF PHASES AT EQUILIBRIUM: ETHYLACETATE - WATER

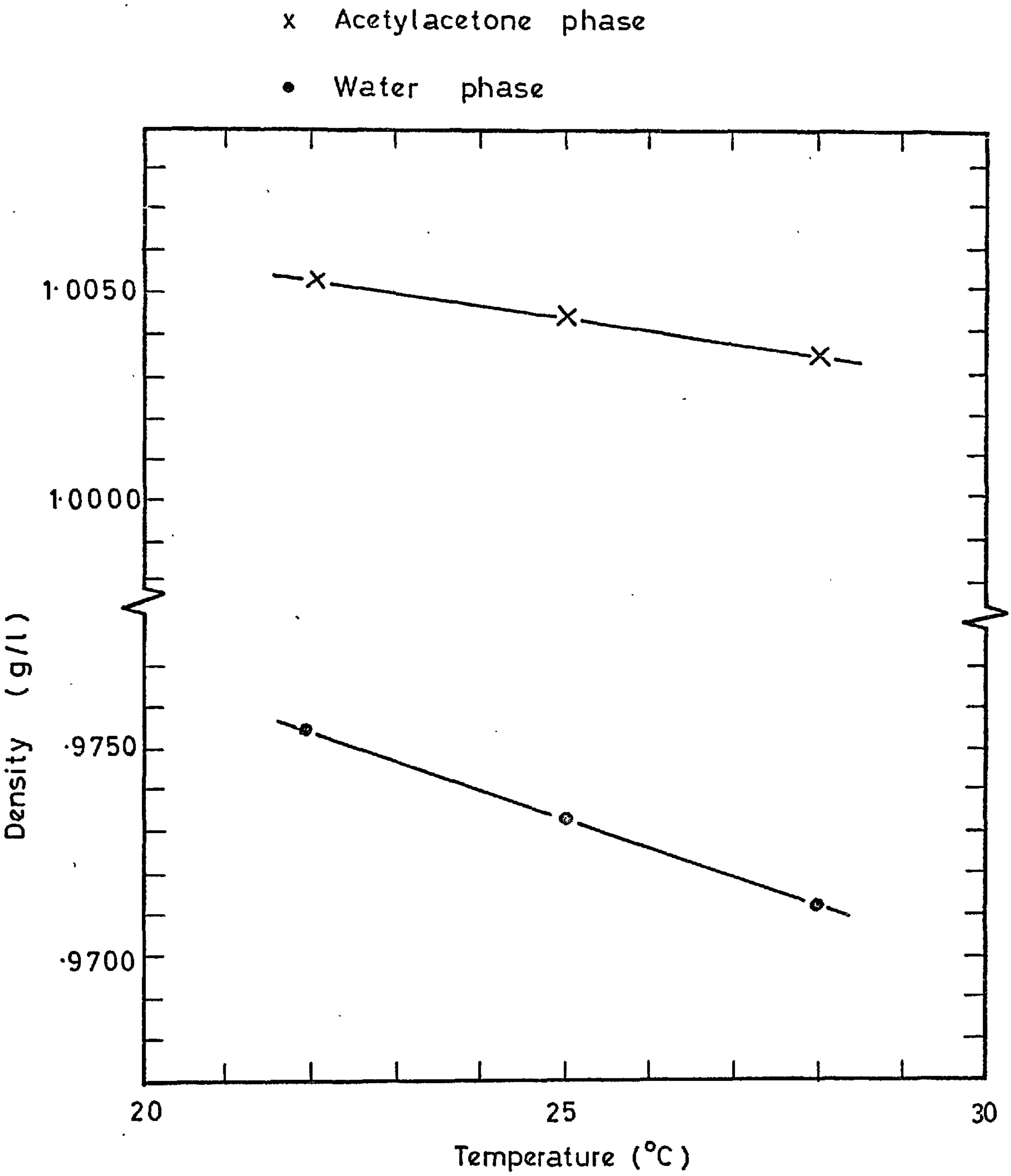


FIG. 5·3 DENSITY OF PHASES AT EQUILIBRIUM: ACETYL ACETONE - WATER.

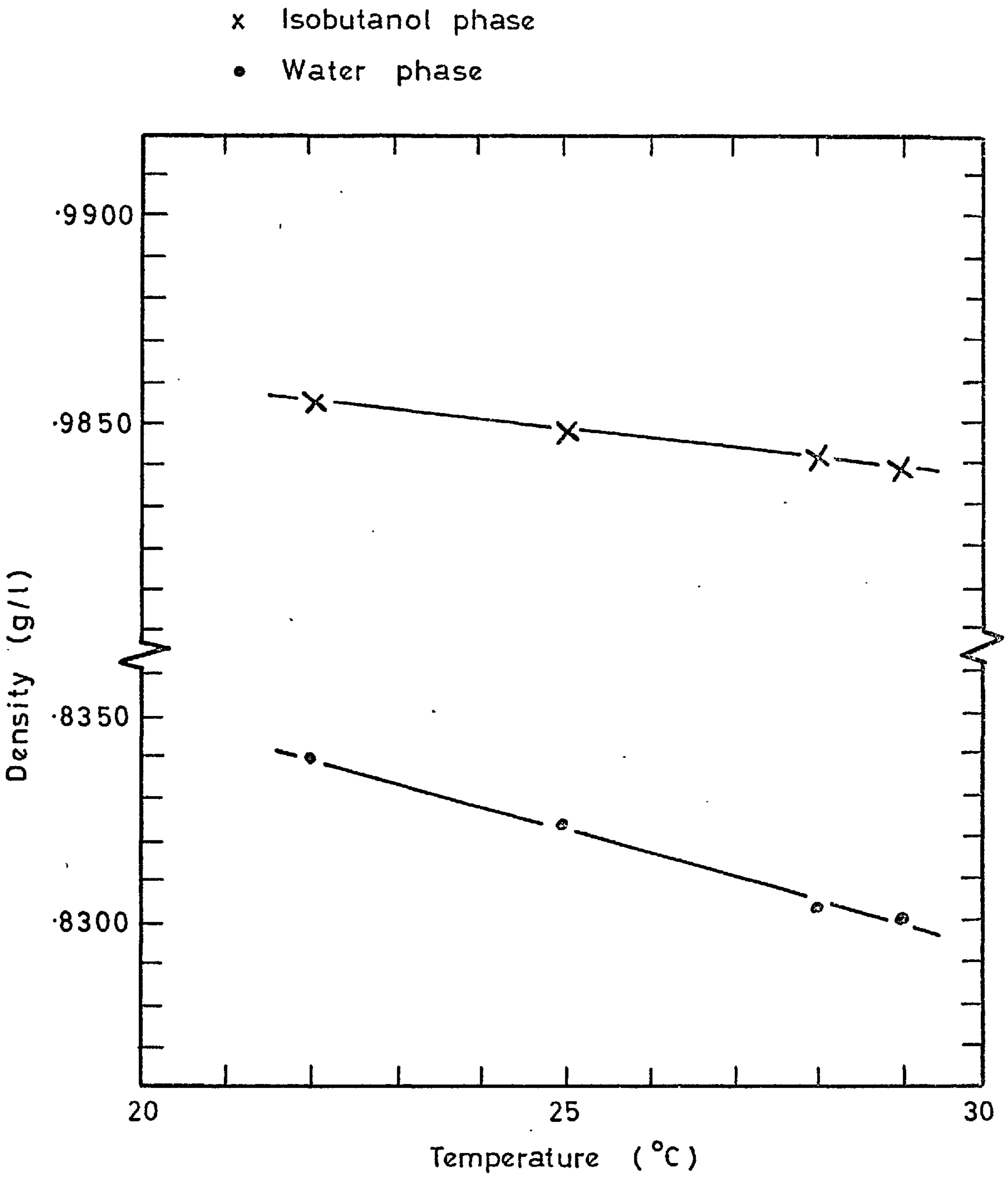


FIG. 5·4 DENSITY OF PHASES AT EQUILIBRIUM: ISOBUTANOL - WATER

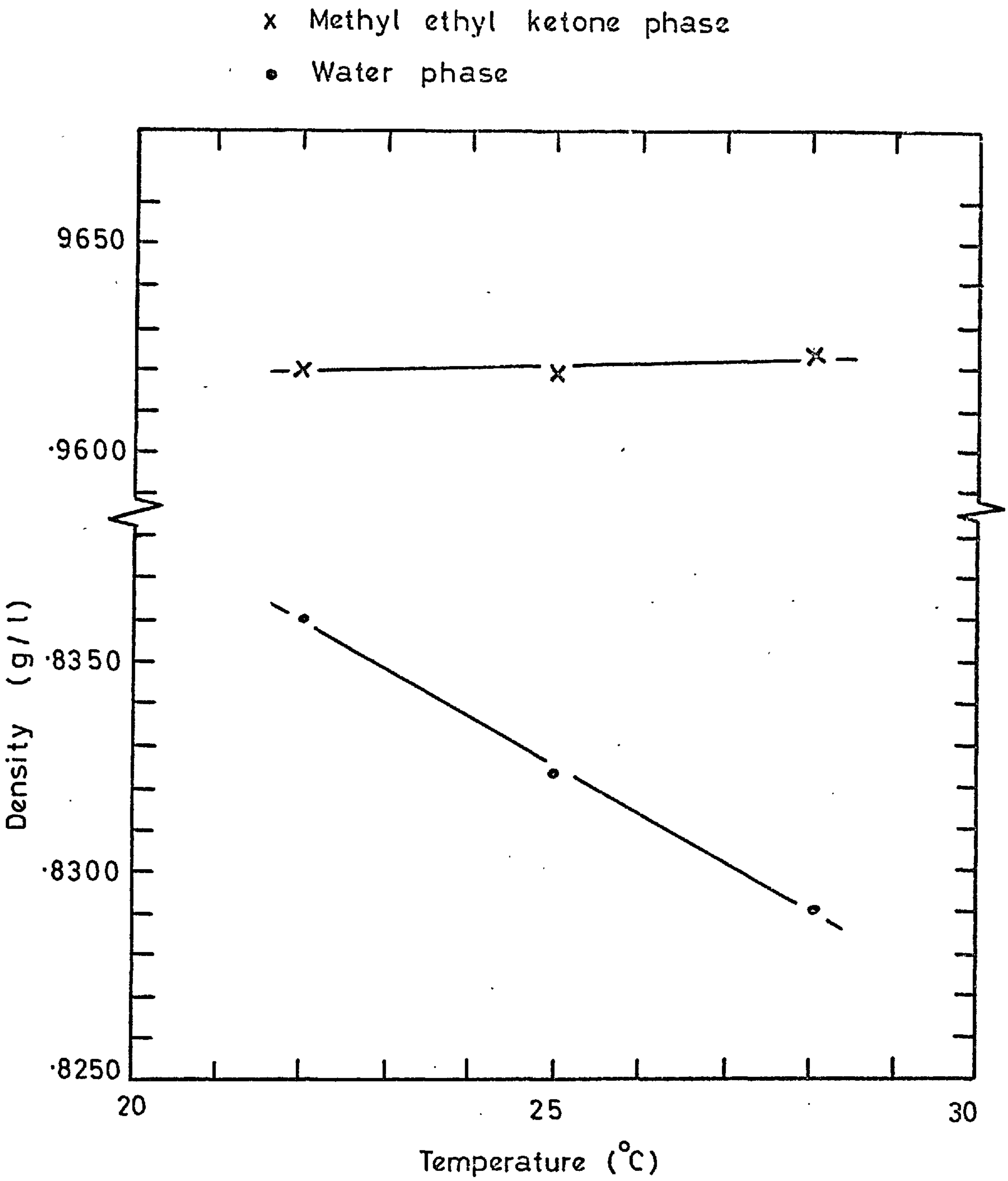


FIG. 5·5 DENSITY OF PHASES AT EQUILIBRIUM: METHYL ETHYL KETONE-WATER.

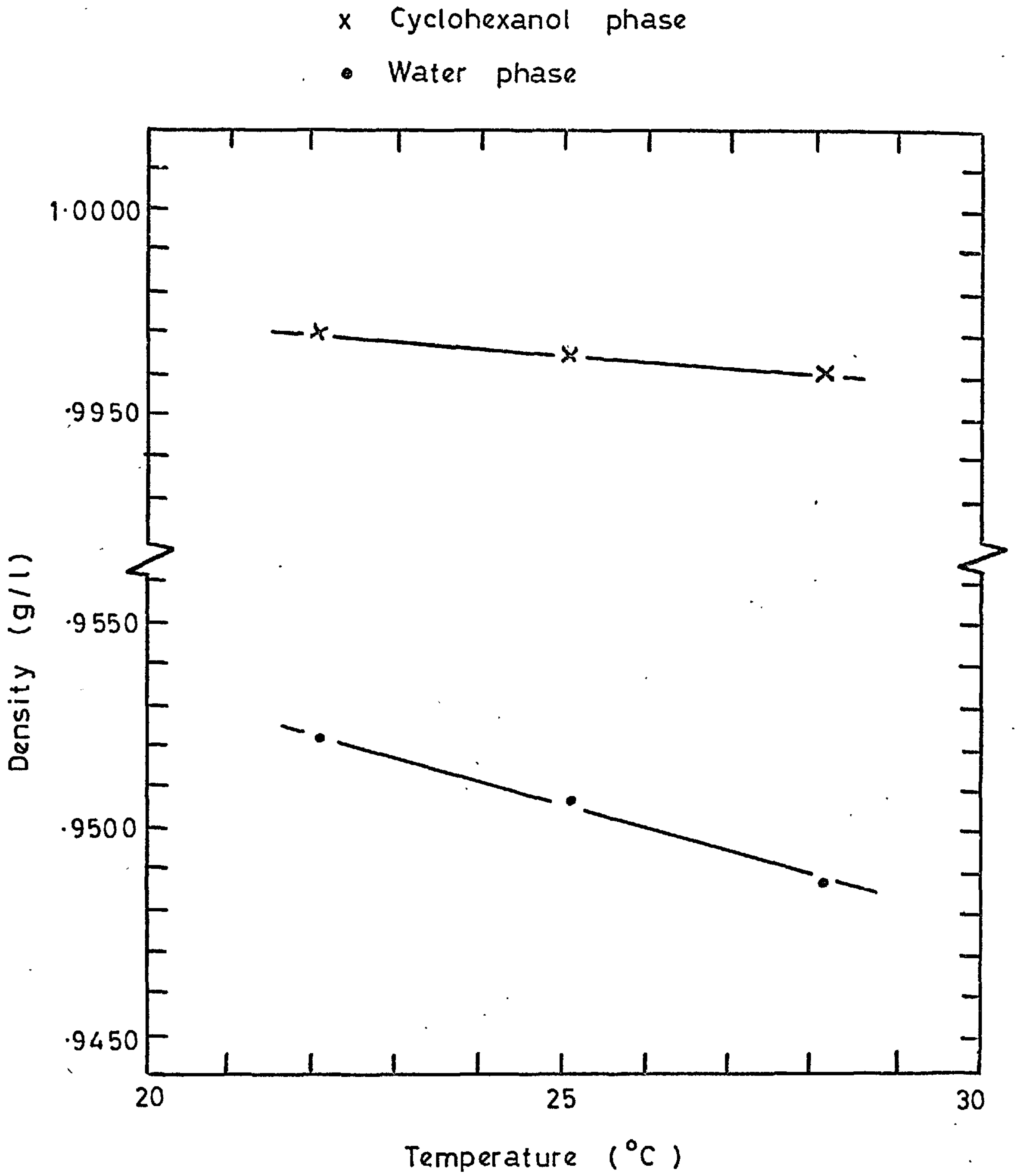


FIG. 5·6 DENSITY OF PHASES AT EQUILIBRIUM: CYCLOHEXANOL - WATER

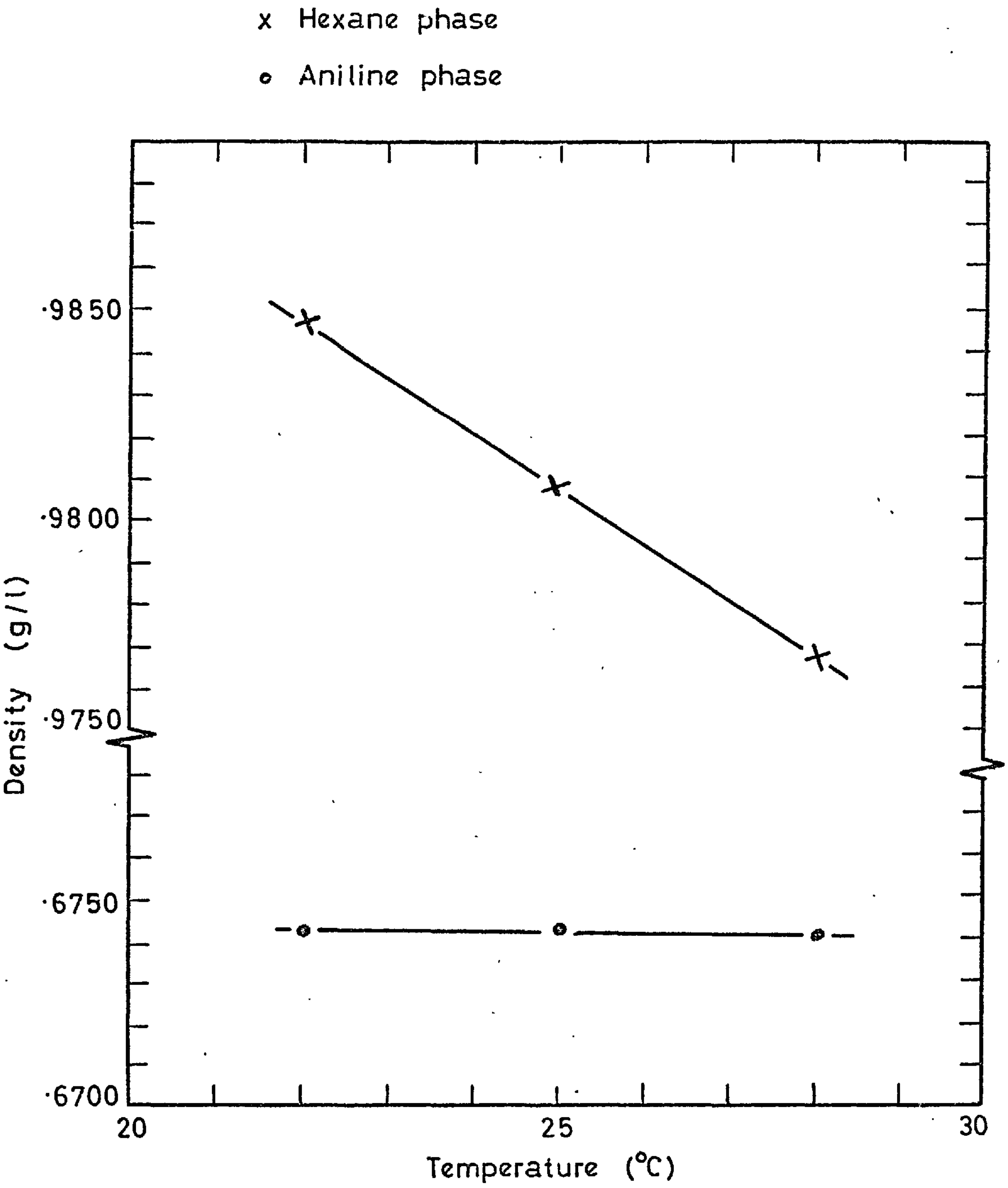


FIG. 5·7 DENSITY OF PHASES AT EQUILIBRIUM: HEXANE - ANILINE

5.2.3 Viscosity

The data on dynamic viscosities for pure and saturated ethyl acetate-water, isobutanol-water, and hexane-aniline pairs were determined by Austin(11), and the data for pure and saturated acetylacetone-water by Atagündüz(42), all at 25 °C. The data for pure cyclohexanol and methyl ethyl ketone were reported in the literature and the corresponding values for the saturated organic and aqueous solutions were calculated with the help of equation (5.1).

5.2.4 Thermal diffusivity

Data available in literature are reported as thermal conductivity. The thermal conductivity of pure acetylacetone and cyclohexanol were calculated using Vargaftik's modification of Palmer's expression(39):

$$k = 1.034\ C_p \rho^{4/3} / a\ \underline{M}^{1/3} \qquad (5.2)$$

where k is expressed in Btu/hft deg F, C_p in Btu/lb deg F and ρ in g/cm^3, and a is an abnormality factor at 30 °C which is defined by:

$$a = \Delta H_{vb} / 21 T_b \qquad (5.3)$$

where ΔH_{vb} = latent heat of vaporization at the normal boiling point, (cal/g mol)

T_b = normal boiling point, °K.

For temperatures other than 30 °C a may be assumed to vary linearly between the value given by equation (5.3) and 1 at the critical temperature. Since for both liquids C_p has been estimated by an approximate equation and a is very close to one, as shown in table 5.2, the temperature correction has not been applied. Equation

(5.2) gives an average and maximum deviation of 8.7 and 31.6 per cent for 28 liquids tested(39). Table 5.2 contains the parameters appearing in equation 5.2 and the results of the calculations for the two liquids.

TABLE 5.2

ESTIMATED THERMAL CONDUCTIVITIES AT 25°C

Solvent	H_{vb}/T_b (cal/gmol°K)	a	$k \times 10^3$ (cal/s cm °C)
Cyclohexanol	25	1.19	0.337
Methyl ethyl ketone	21.7	1.03	0.407

The data for all the other pure liquids are experimental measurements reported in literature.

The values of the thermal diffusivities were calculated from its definition:

$$K = k/\rho C_p$$

5.2.5 Mass diffusivity

Austin and Sawistowski(11) reviewed the semi-empirical correlations for the prediction of diffusion coefficients. They concluded that Sitaraman's(47) correlation is the most consistent of those investigated in that the predicted values of $D\mu/T$ at infinite dilution are in reasonable agreement with literature values. Consequently, Sitaraman's correlation was adopted in the present work. The correlation fits the data with a standard deviation of 26% by:

$$D_{AB} = 5.4 \times 10^{-8} \left[\frac{M_B \, \Delta H_{VB}/\underline{M}_B)^{1/3} \quad T}{\mu_B \, (\Delta H_{VA}/\underline{M}_A)^{0.3} \quad v_A{}^{1/2}} \right]^{0.93} \qquad (5.4)$$

where v_A = molecular volume of the solute A(49),

D_{AB} = diffusivity of A in B, cm^2/s

Garner and Marchant(48) have shown that $D\mu/T$ for the diffusion of isobutanol in water is virtually independent of concentration. In the absence of experimental data the other systems were assumed to have the same property. The results of the computations made with equation (5.4) are contained in table B4, appendix B.

5.2.6 Equilibrium concentration and its variation with temperature

The literature was searched for solubility data as a function of temperature for the selected systems and the results are plotted in appendix B, figures B1 to B6. Solubility data at 25 °C and rate of change of equilibrium concentration with temperature are estimated from these curves and presented in table B5, appendix B.

5.2.7 Heat of solution

In the absence of experimental data on heats of solution of water in ethyl acetate, acetyl acetone, isobutanol and cyclohexanol, they were measured by the Imperial College Analytical Services Laboratory. The heats of solution of aniline into hexane and hexane into aniline were measured as well because the data reported by Keyes and Hildebrand(50) are, in the authors' own words, "rough determinations".

TABLE 5.3

INTEGRAL HEATS OF SOLUTION

Solvent	Solute	T °C	Q^o cal/gmol solute	standard deviation
ethyl acetate	water	25	-1150	18.9
acetylacetone	water	25	-1018	23.8
isobutanol	water	25	-295	14.8
cyclohexanol	water	25	-234	4.76
hexane	aniline	19	-1320	21.1
aniline	hexane	25	-1170	19.3

The results presented in table 5.3 are the quantity of heat absorbed by the solution when the amount of solute necessary to get a saturated solution is added to the pure solvent. The results are the average of three determinations.

5.2.8 Interfacial tension

Except for the system isobutanol-water no data on the effect of temperature on interfacial tension were found in the literature. Consequently, the equilibrium interfacial tensions at different temperatures were measured. The determinations were made by the drop-weight volume method. Figure 5.8 shows a diagram of the apparatus. It consists of a capillary U-tube ACD with a bulb at B and a detachable tip T at D which is projected into a glass vial F. The tip is attached to the capillary tube by means of a cone and socket joint. The volume of the bulb and of the capillary joining it to the graduated sections of capillary tube, AB and BC, was accurately known to be 2.338 ml.

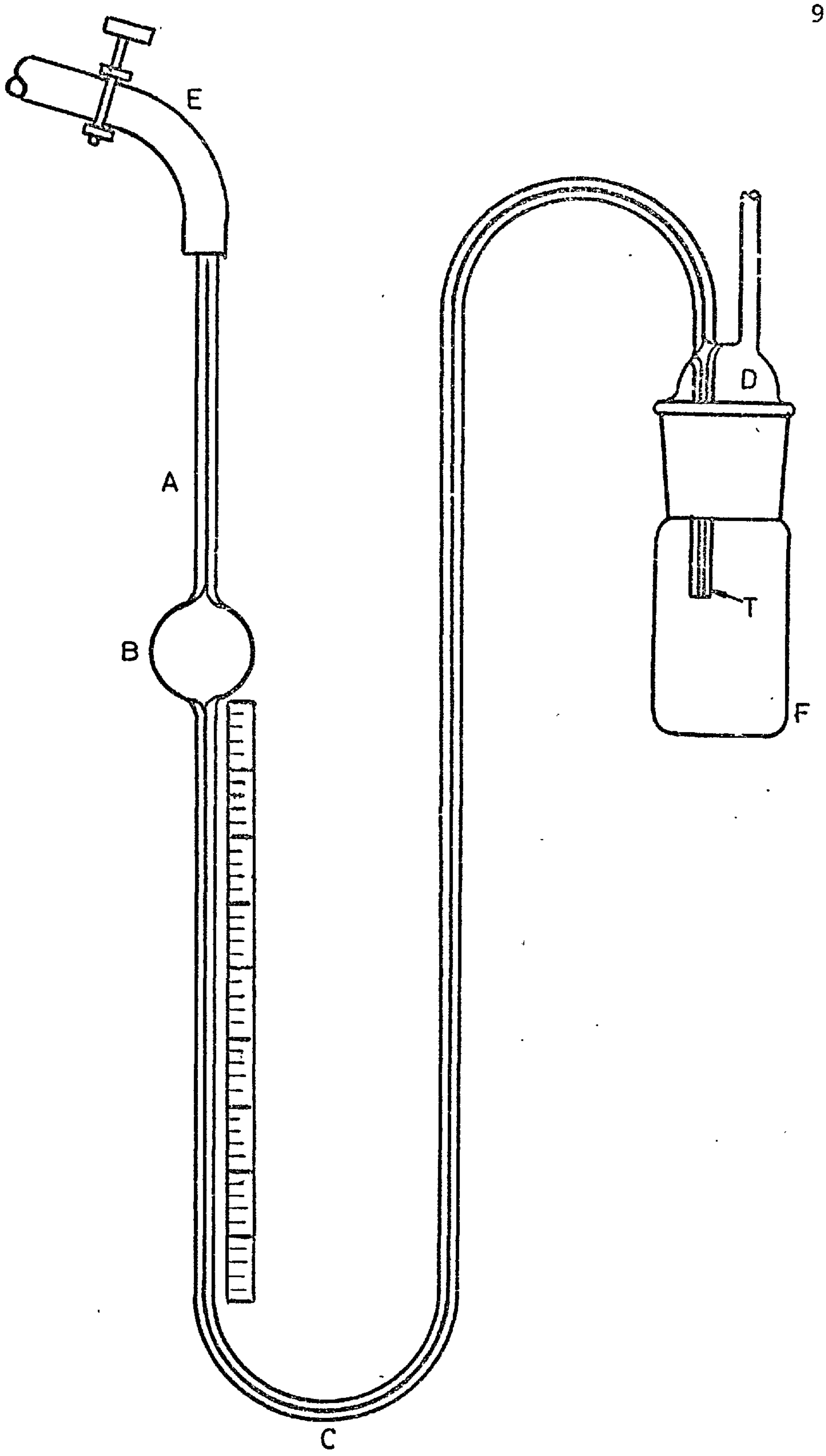


FIG. 5·8 THE PENDENT DROP APPARATUS

The heavier phase was sucked up into the capillary until the level reached the graduated section AB and the clip was tightened. The lighter phase was poured into the vial so that the tip was just covered when the vial was clamped in position. The apparatus was supported vertically, by means of a support rod s, in a thermostat both controlled at 22, 25 or 28 ± 0.05 °C. The interface was adjusted to the plane of the tip and the level noted in the graduated capillary AB. Drops were formed until the level was positioned in the lower capillary BC, the interface was again adjusted to the plane of the tip and the level in BC noted. The drops were formed at a rate of about one a minute, the last 10% of the drops being delivered very slowly to ensure that the drop detached under the influence of gravity alone.

The mean drop value was calculated from the total volume and the number of drops. The interfacial tension was then calculated from the equation:

$$\sigma_{D} = \frac{V(\rho_B - \rho_A)\, g}{2\Pi\, r_t\, f(r/V^{1/3})} \qquad (5.4)$$

where: V = mean drop volume (cm^3)

$\rho_A \rho_B$ = densities of the lighter and heavier phases respectively (g/cm^3)

g = acceleration due to gravity (cm/s^2)

r_t = wetted radius of the tip (cm).

$f(r/V^{1/3})$ = correction factor (51).

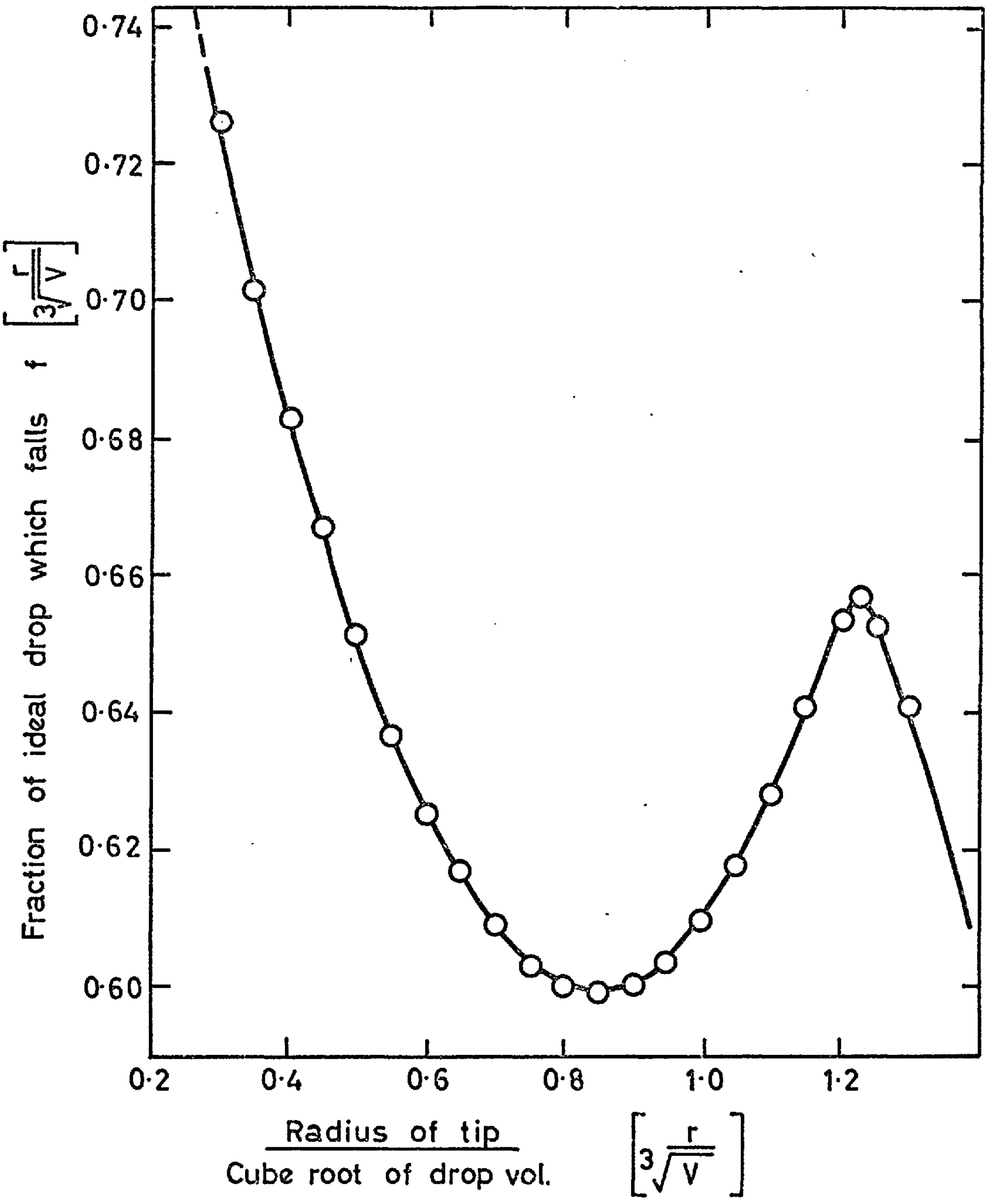


FIG. 5·9 HARKINS CORRECTION FACTOR, EQ.^{N} 6·3

The correction factor is applied to allow for the fact that the liquid forming the drop does not completely leave the tip. This factor is a function of the wetted radius of the tip and the cube root of the drop volume (figure 5.9) and is accurately known for $0.3 < r_t V^{1/3} < 1.2$. Two tip diameters were chosen so that the resulting values of $r_t V^{1/3}$ for the systems fell within the above limits. The tips were made from Veridia precision tubing and ground flat and square using the method of Harkins and Brown(52).

Before use the capillary, tip and vial were soaked in chromic-sulphuric acid, washed with distilled water and acetone and finally air dried. The readings are tabulated in table B6, appendix B, and the results presented in Figures 5.10 and 5.11. Table 5.4 contains the experimental results obtained for the system isobutanol-water and also data from literature. There is not much difference between the results of the present work and the data measured by Austin(11). Silbereisen(15) measured the interfacial tension with the de Noüy method and this could be the explanation of the greater difference between his results and this work. However, there is agreement in the sign of the variation of interfacial tension with temperature, which is the main purpose of the experimental determinations in this work.

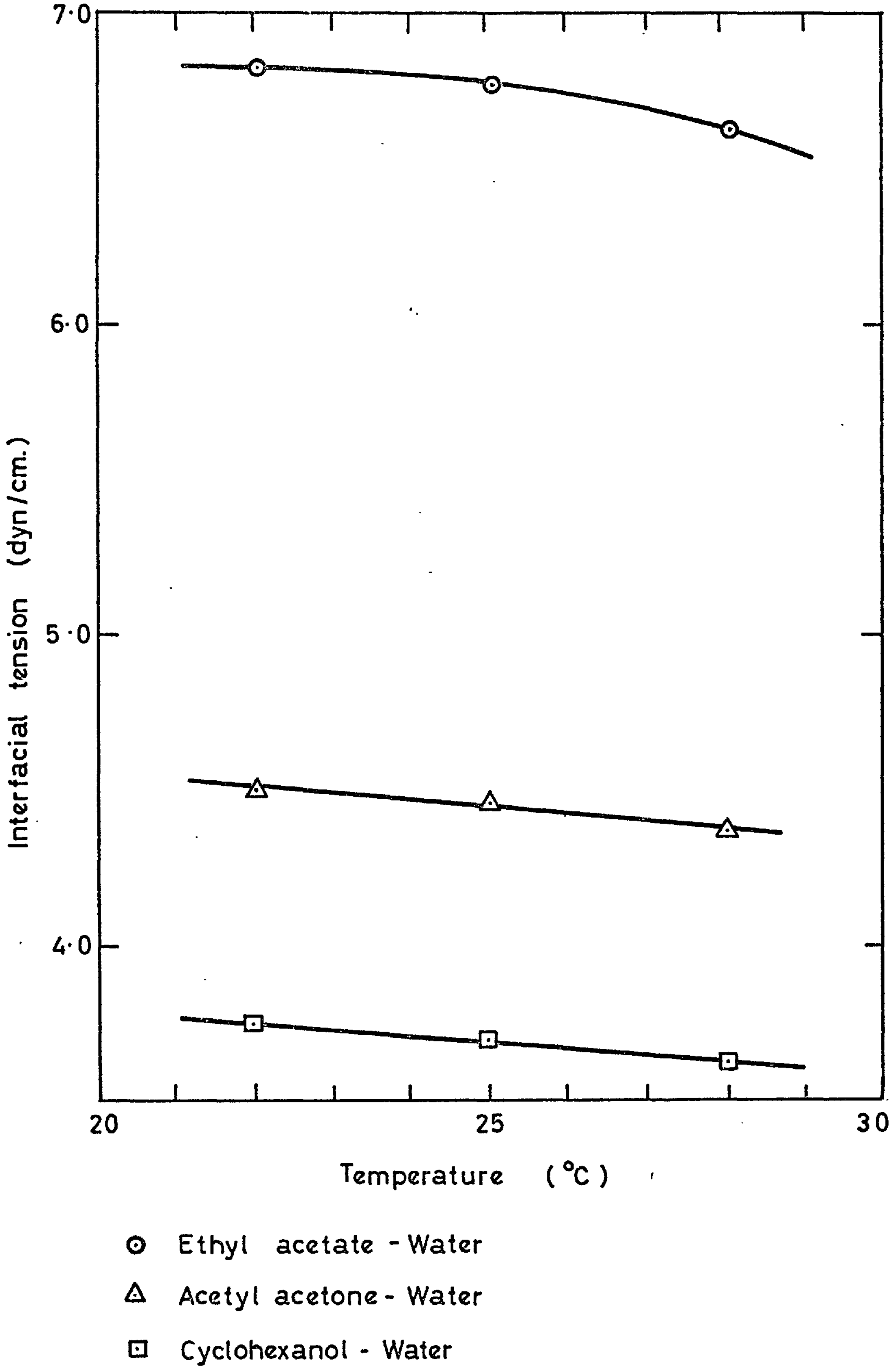


FIG. 5·10 INTERFACIAL TENSION vs. TEMPERATURE

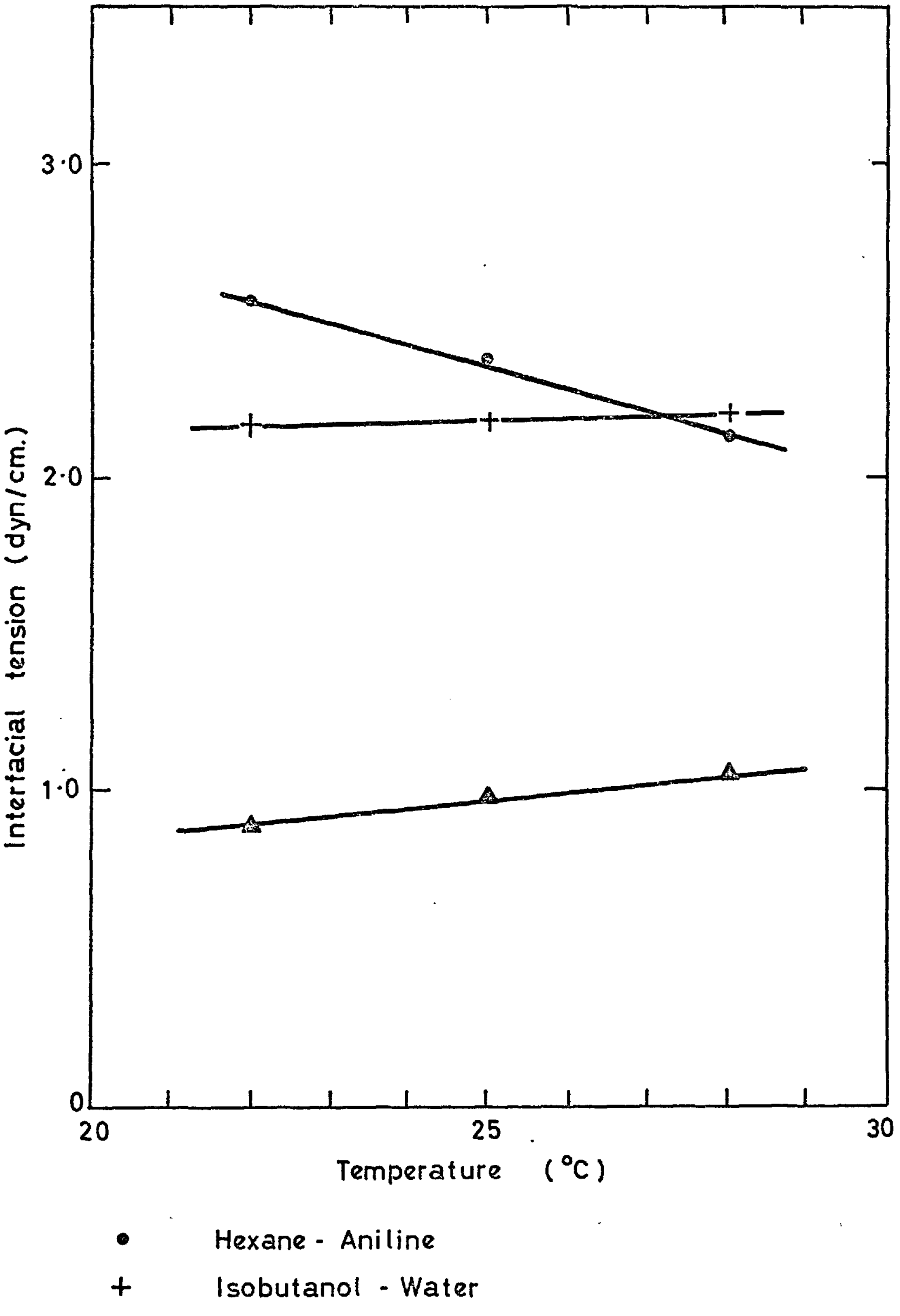


FIG. 5·11 INTERFACIAL TENSION vs TEMPERATURE

TABLE 5.4

EFFECT OF TEMPERATURE ON INTERFACIAL TENSION IN THE SYSTEM ISOBUTANOL-WATER

T	This work	Literature	Reference
	σ_i	σ_i	
^oC	dyn/cm	dyn/cm	
17		1.78	(15)
22	2.15	1.85	(15)
25	2.17	2.2	(11)
28	2.18	1.86	(15)

5.3 Temperature and concentration profiles

The time dependent temperature and concentration profiles were calculated with equations 3.44 to 3.47 using the Imperial College CDC 6400 system. The results after 30 seconds of contacting the phases initially at 25 ^oC are plotted in figures 5.14 to 5.25 (a) and (b). Figure 5.13 shows the temperature and concentration profiles in the system methyl ethyl ketone-water at intervals of 20 seconds after contacting the phases when water is transferred from the saturated water phase to pure methyl ethyl ketone.

In order to apply the characteristic equation to the study of the selected systems, the profiles have to be linearised. The validity of this procedure is discussed in section 5.4. Since the stability of the systems will be analysed in turn with respect to each direction of transfer separately, equation (4.67) will be used and only the temperature profiles need be linearised.

The standard technique of linearization (Vidal and Acrivos (31), Lick (33)) is to approximate the actual profile with a straight-line segment, figure 5.12, so that the area under the curve in figure 5.12(a) is the same as the area of the triangle in figure 5.12(b). Then, the effective thermal depth is:

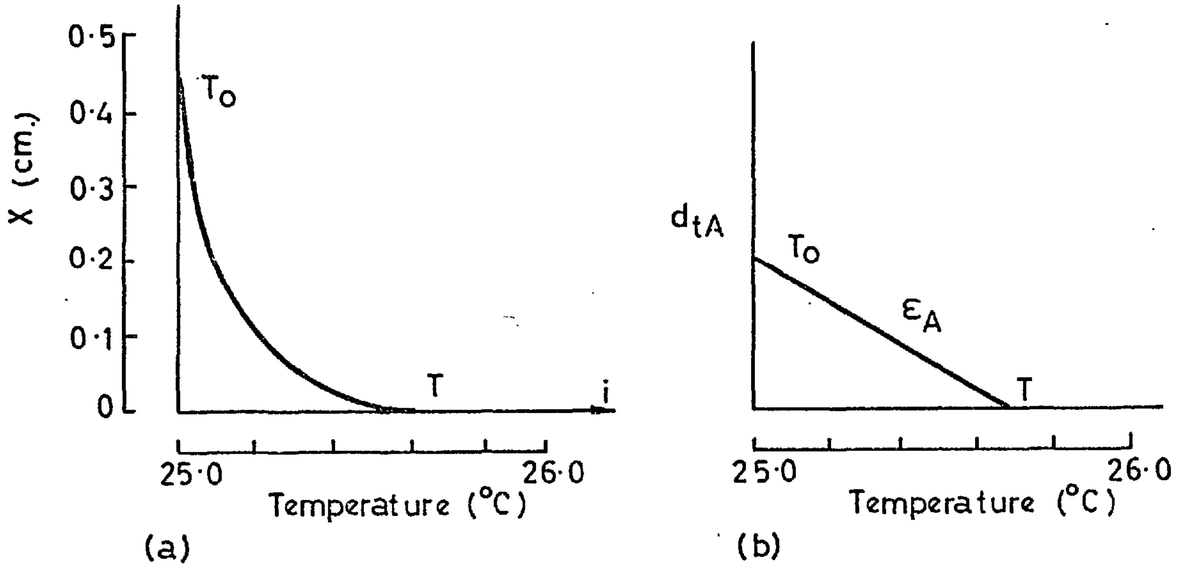


FIG. 5·12 DEFINITION OF APPROXIMATE TEMPERATURE PROFILE

$$d_{tA} = \frac{2\int_{o}^{d_{oA}} T_A(x,t)\ dx_A}{T_i - T_o}, \qquad x \geqslant 0 \qquad (5.5)$$

$$d_{t_B} = \frac{2\int_{o}^{-d_{oB}} T_B(x,t)dx_B}{T_i - T_o}, \qquad x < 0 \qquad (5.6)$$

where d_o is the adopted depth of the phase. For the case under consideration the value of d_o was arbitary, being governed by only one condition that the points $x = d_{oA}$ and $x = d_{oB}$ were at $T = T_o$.

The integrals in equations (5.5) and (5.6) were calculated at $t = 30$ seconds for $d_{oA} = d_{oB} = 1$ cm.

Figures 5.14 to 5.25 show that at a depth of 1 cm from the interface, the temperature in both phases is 25 °C. The integrals were calculated with the trapezoidal quadrature formula with error control, which is the more adequate to integrate the error function in equations (3.46) and (3.47).

The linear temperature profiles are calculated by:

$$\varepsilon_A = (T_o - T_2)/d_{tA} \tag{5.7}$$

$$\epsilon_B = (T_o - T_i)d_{tB} \tag{5.8}$$

The linearised temperature profiles are shown in figures 5.14 to 5.25 (c).

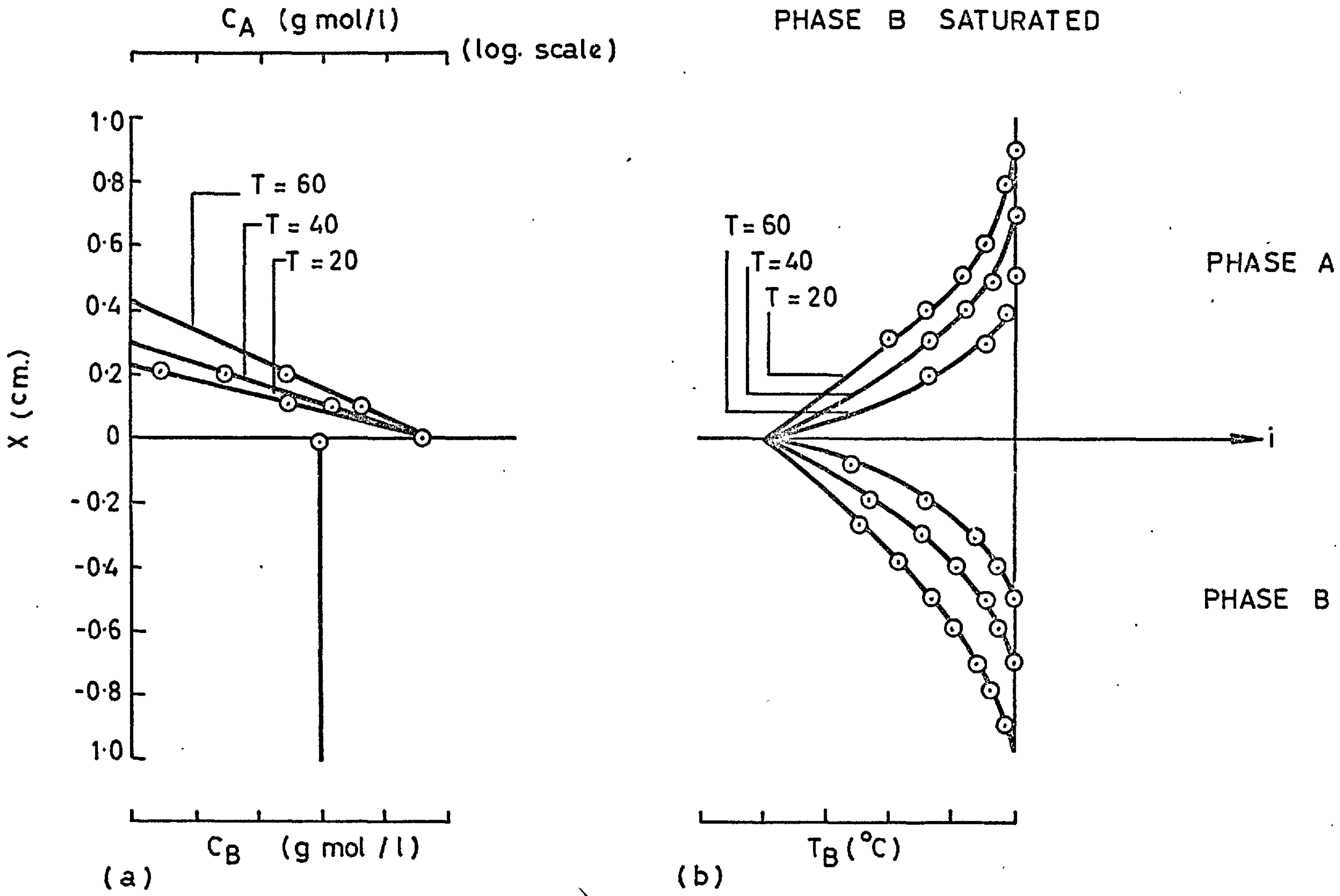


FIG. 5·13 CONCENTRATION AND TEMPERATURE PROFILES AT DIFFERENT TIMES OF CONTACT: SYSTEM METHYL ETHYL KETONE-WATER.

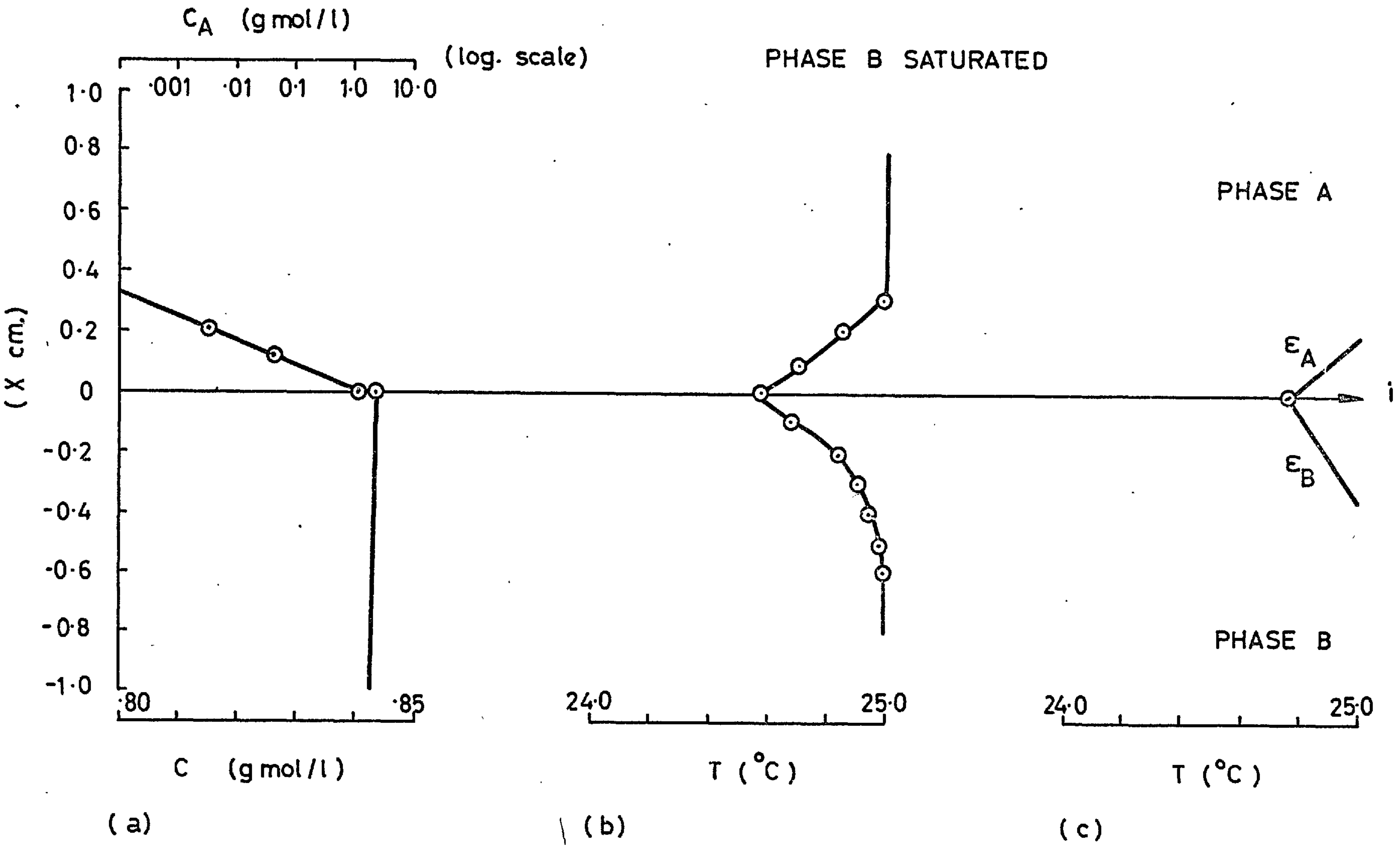


FIG. 5·14 CONCENTRATION AND TEMPERATURE PROFILES: SYSTEM ETHYLACETATE - WATER

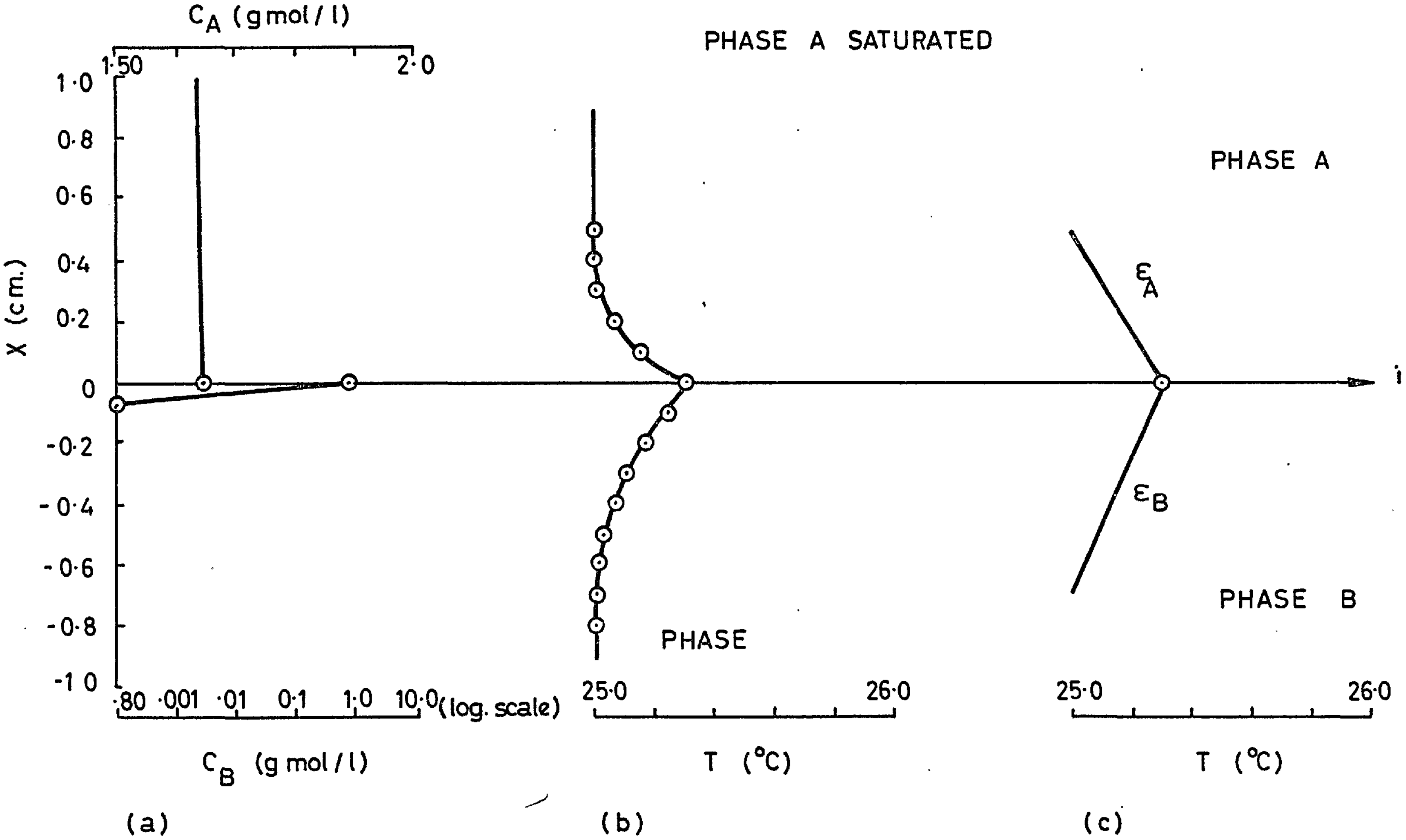


FIG. 5·15 CONCENTRATION AND TEMPERATURE PROFILES: ETHYLACETATE - WATER

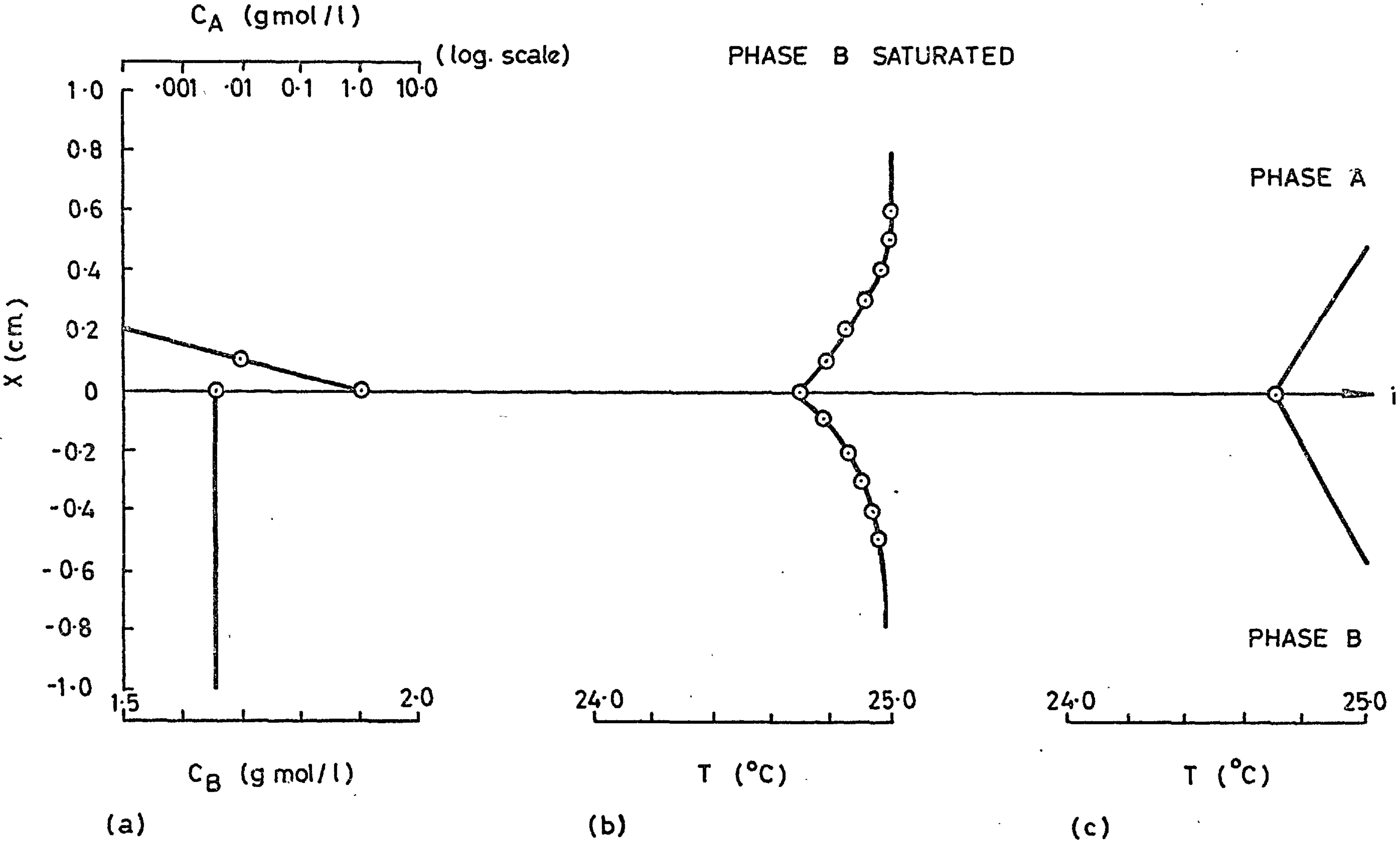


FIG. 5·16 CONCENTRATION AND TEMPERATURE PROFILES: ACETYLACETONE - WATER

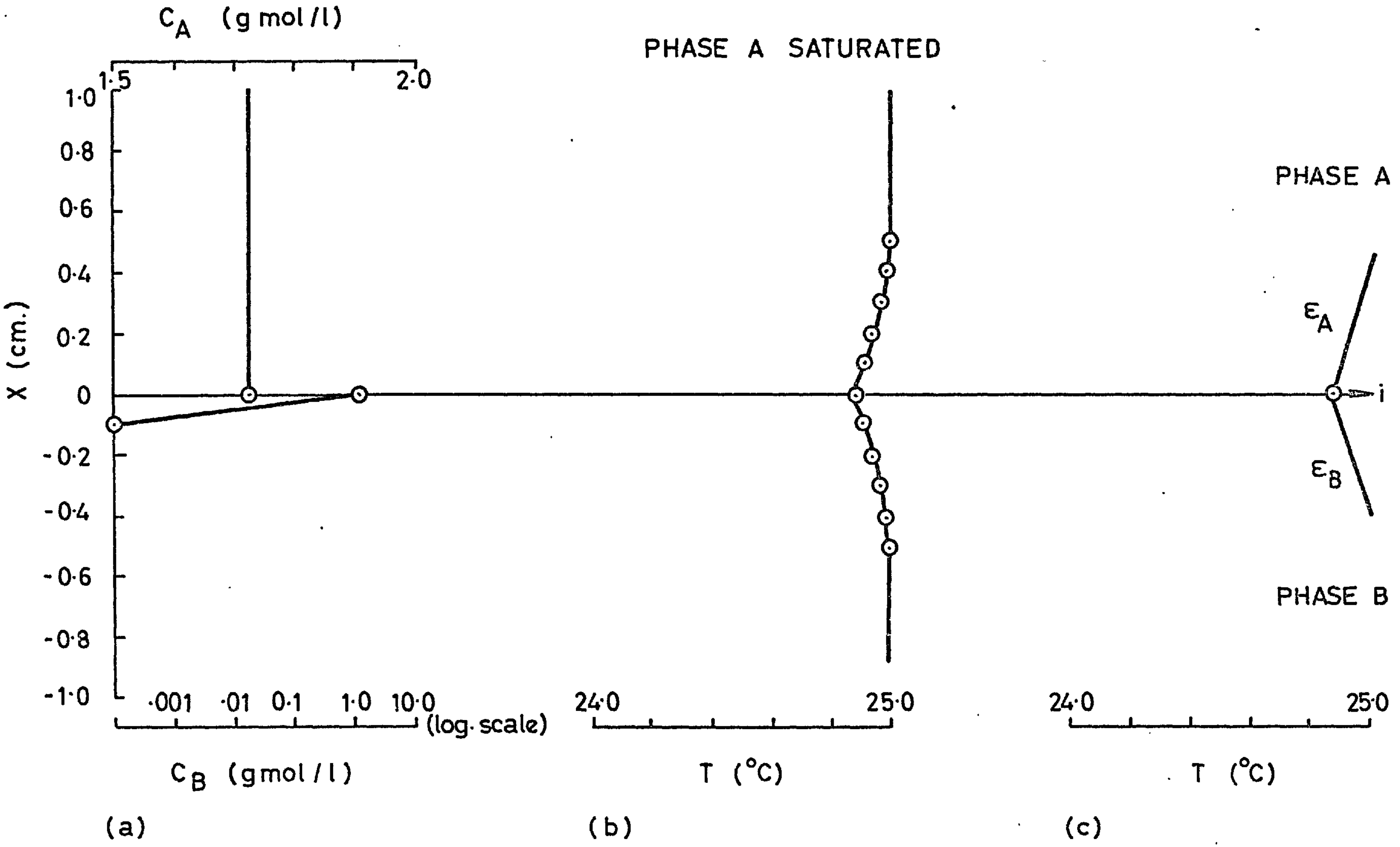
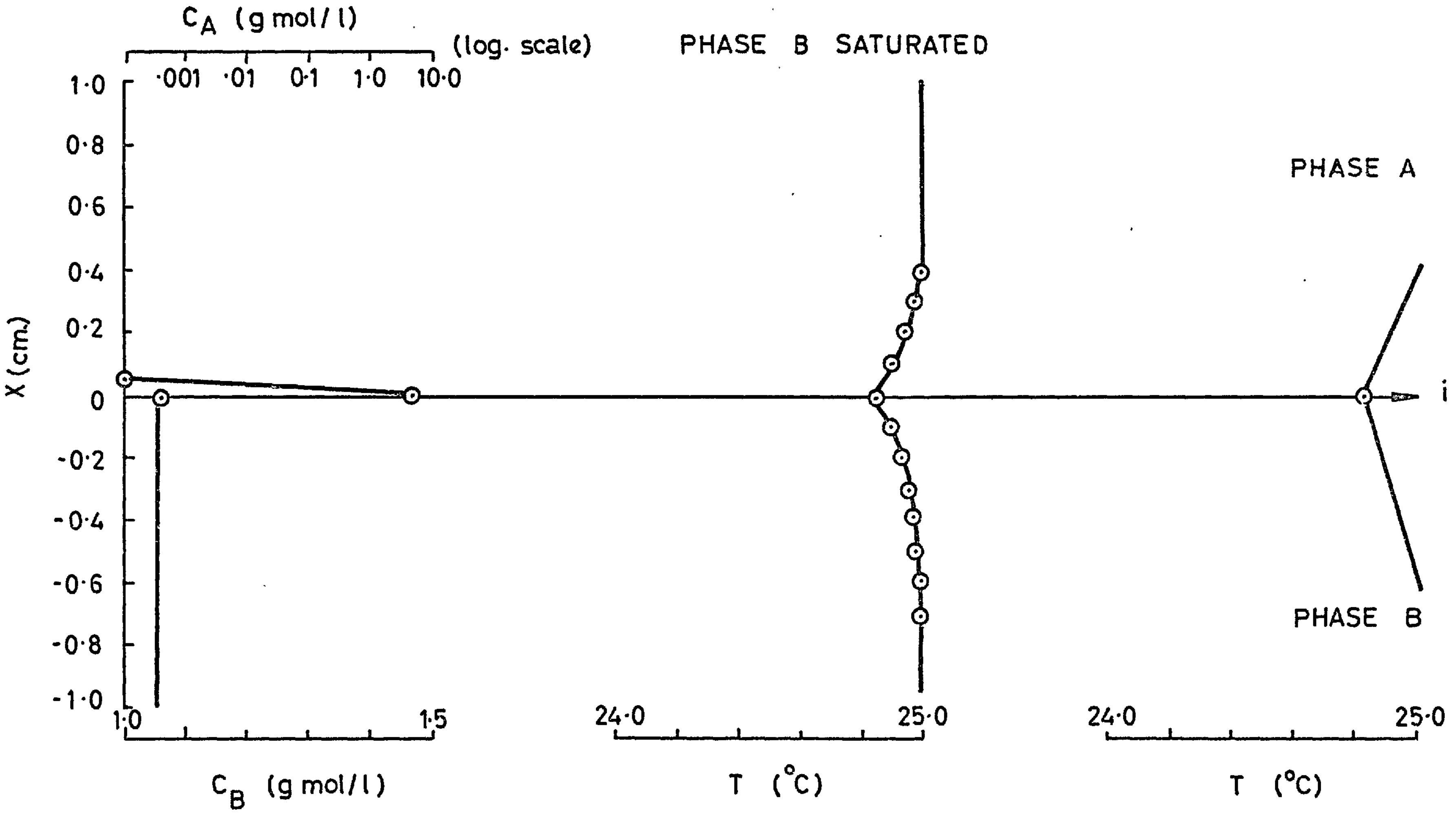


FIG. 5·17 CONCENTRATION AND TEMPERATURE PROFILES: ACETYLACETONE - WATER



(a) (b) (c)

FIG. 5·18 CONCENTRATION AND TEMPERATURE PROFILES: ISOBUTANOL - WATER

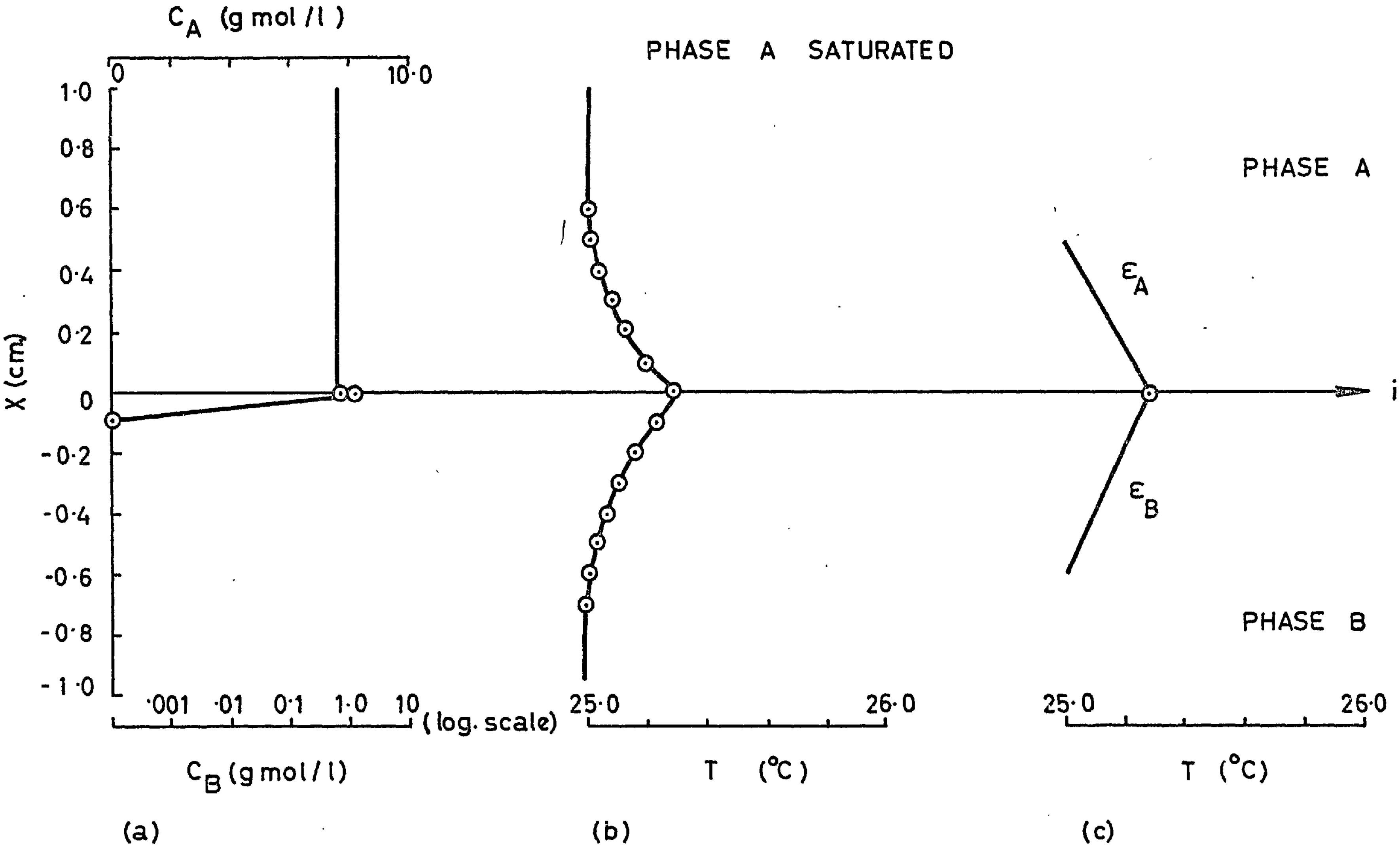


FIG. 5·19 CONCENTRATION AND TEMPERATURE PROFILES: ISOBUTANOL - WATER

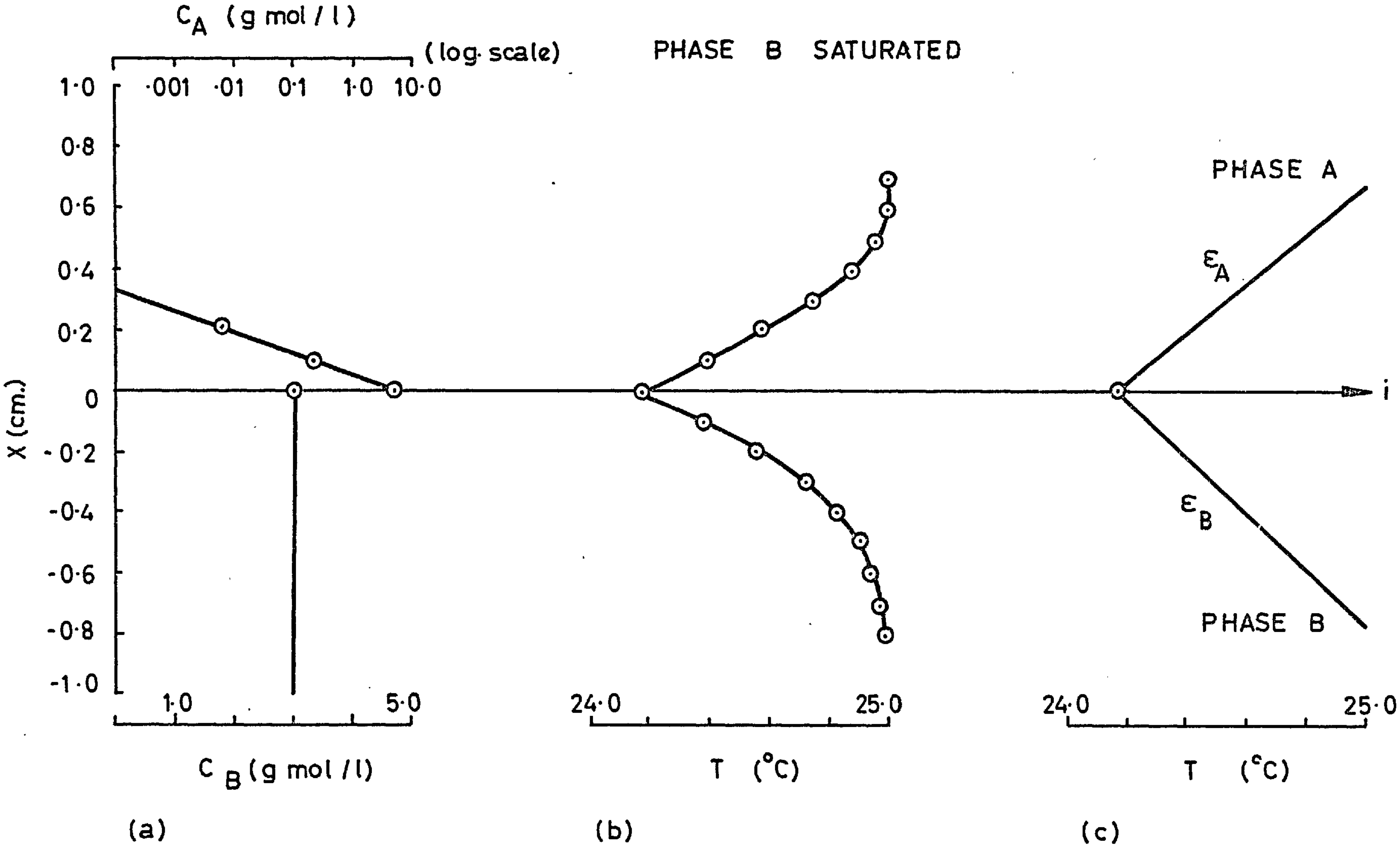


FIG. 5·20 CONCENTRATION AND TEMPERATURE PROFILES: METHYL ETHYL KETONE-WATER

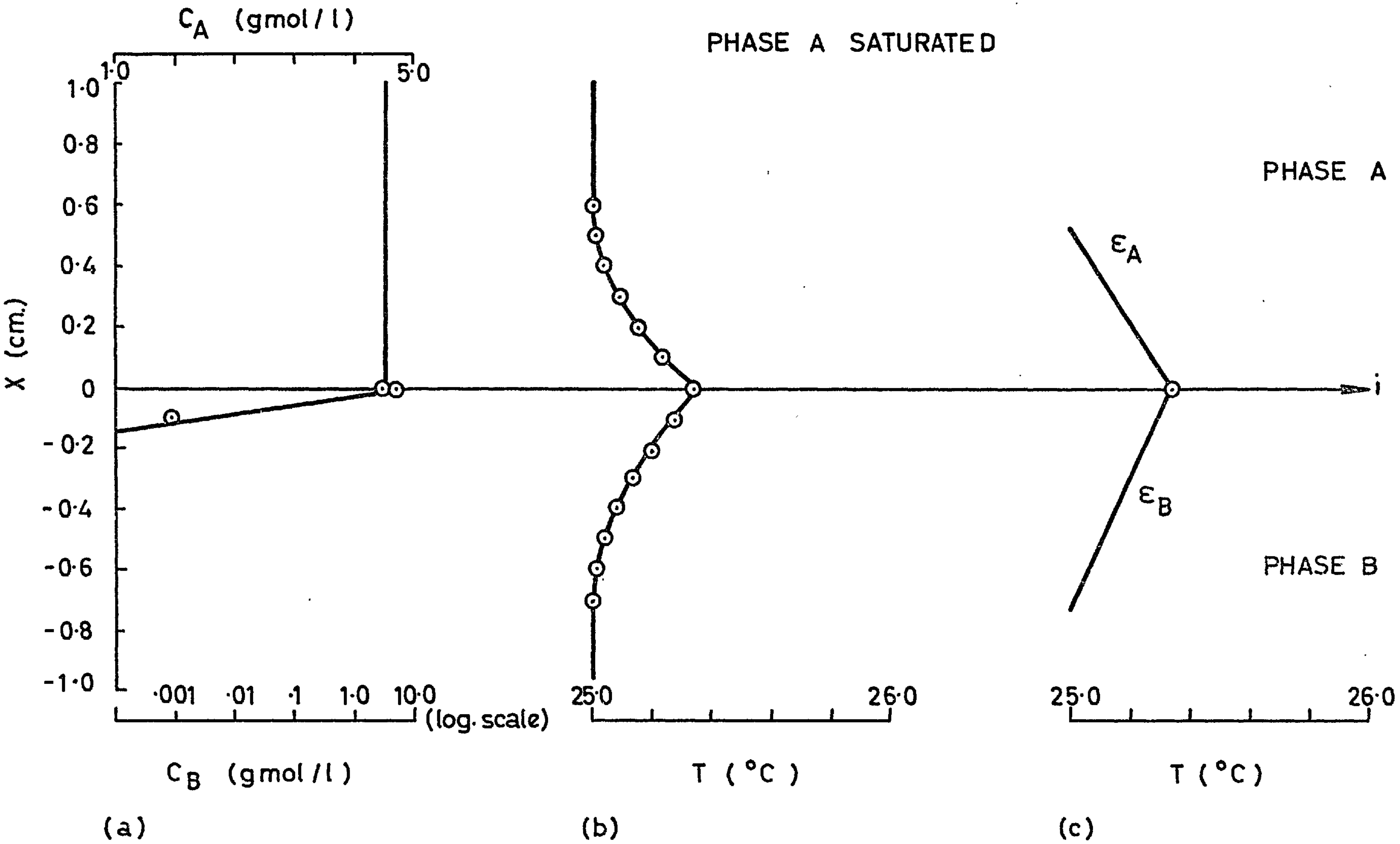


FIG. 5·21 CONCENTRATION AND TEMPERATURE PROFILES METHYL ETHYL KETONE - WATER

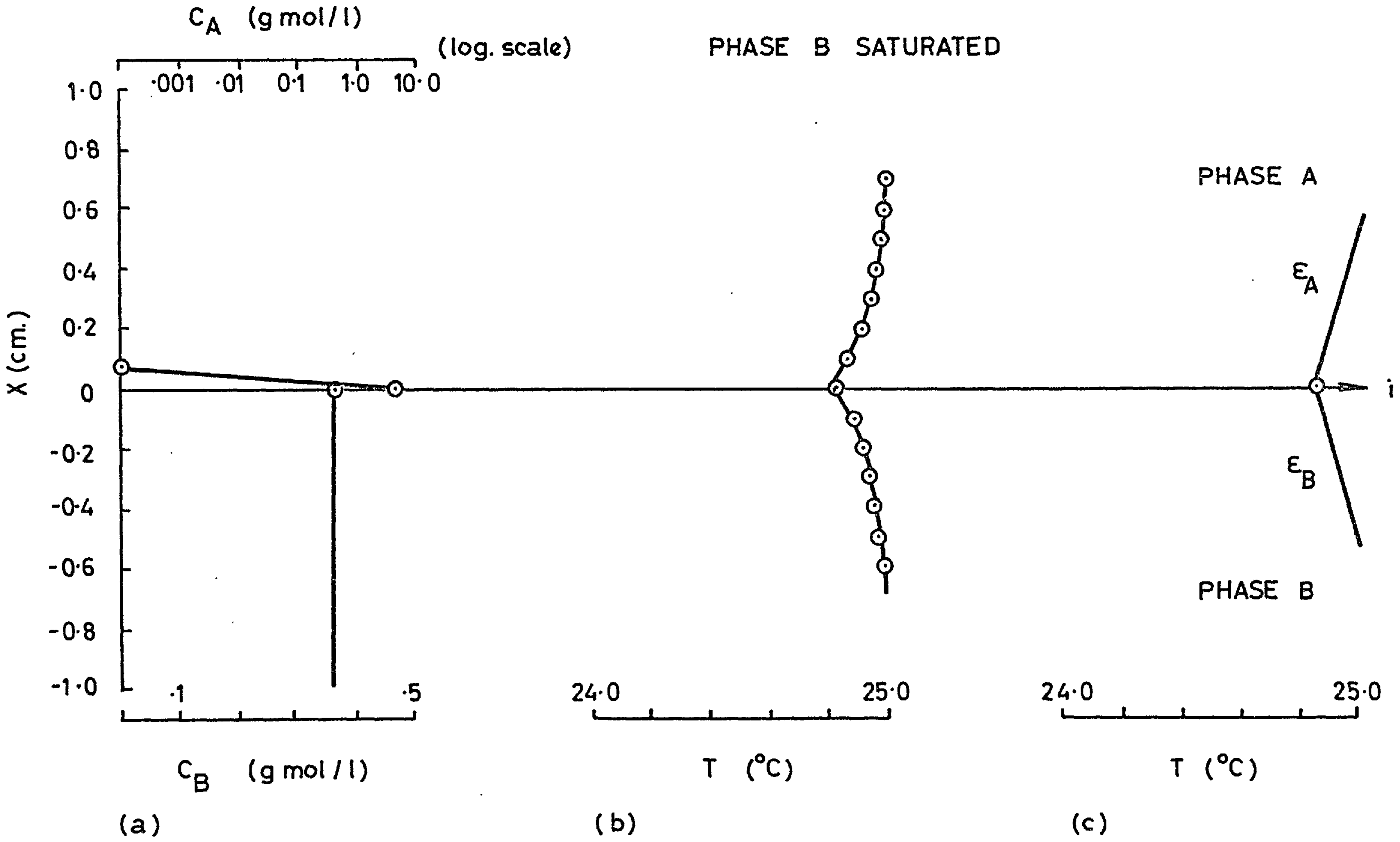


FIG. 5·22 CONCENTRATION AND TEMPERATURE PROFILES: CYCLOHEXANOL - WATER

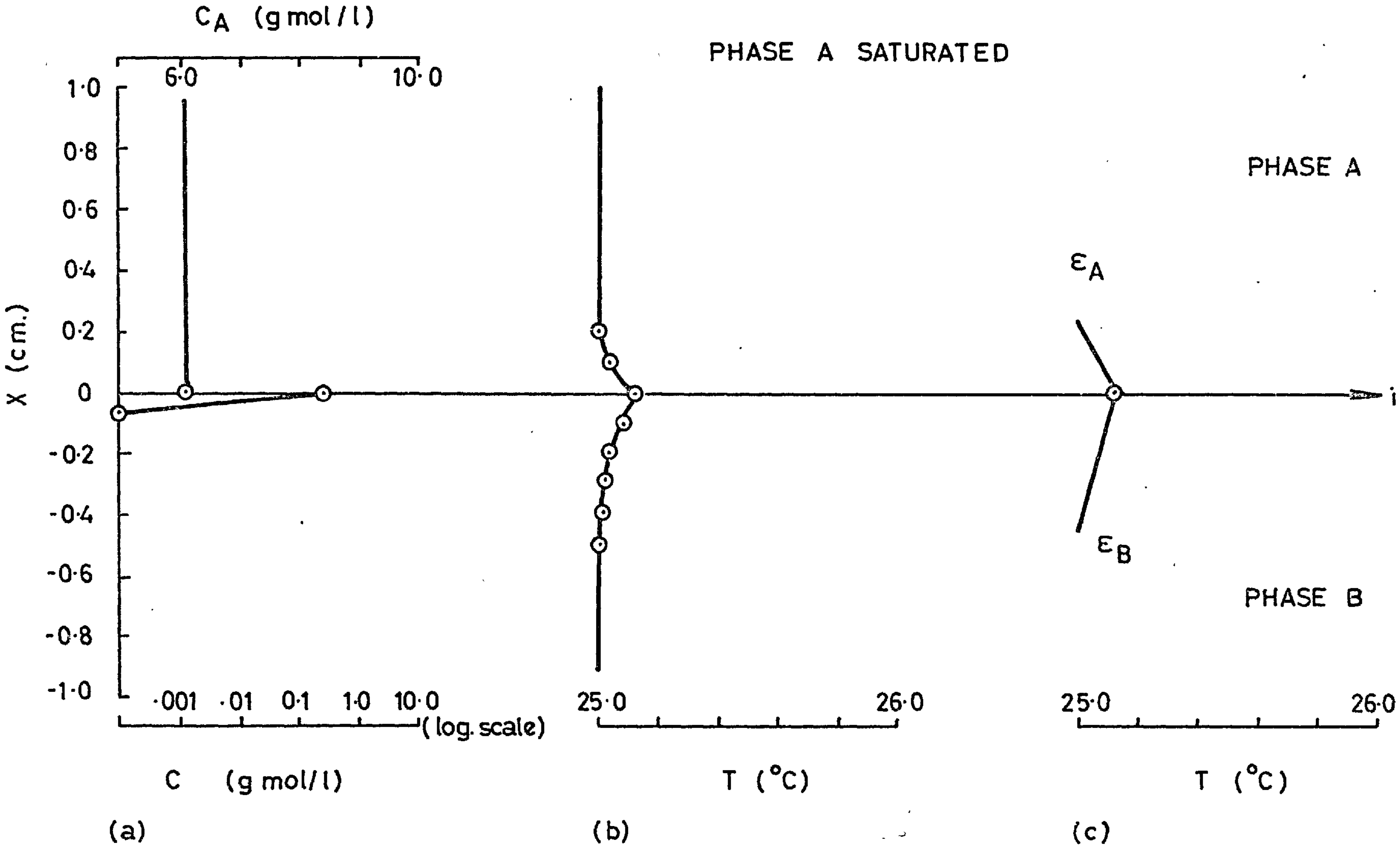


FIG. 5·23 CONCENTRATION AND TEMPERATURE PROFILES: CYCLOHEXANOL - WATER

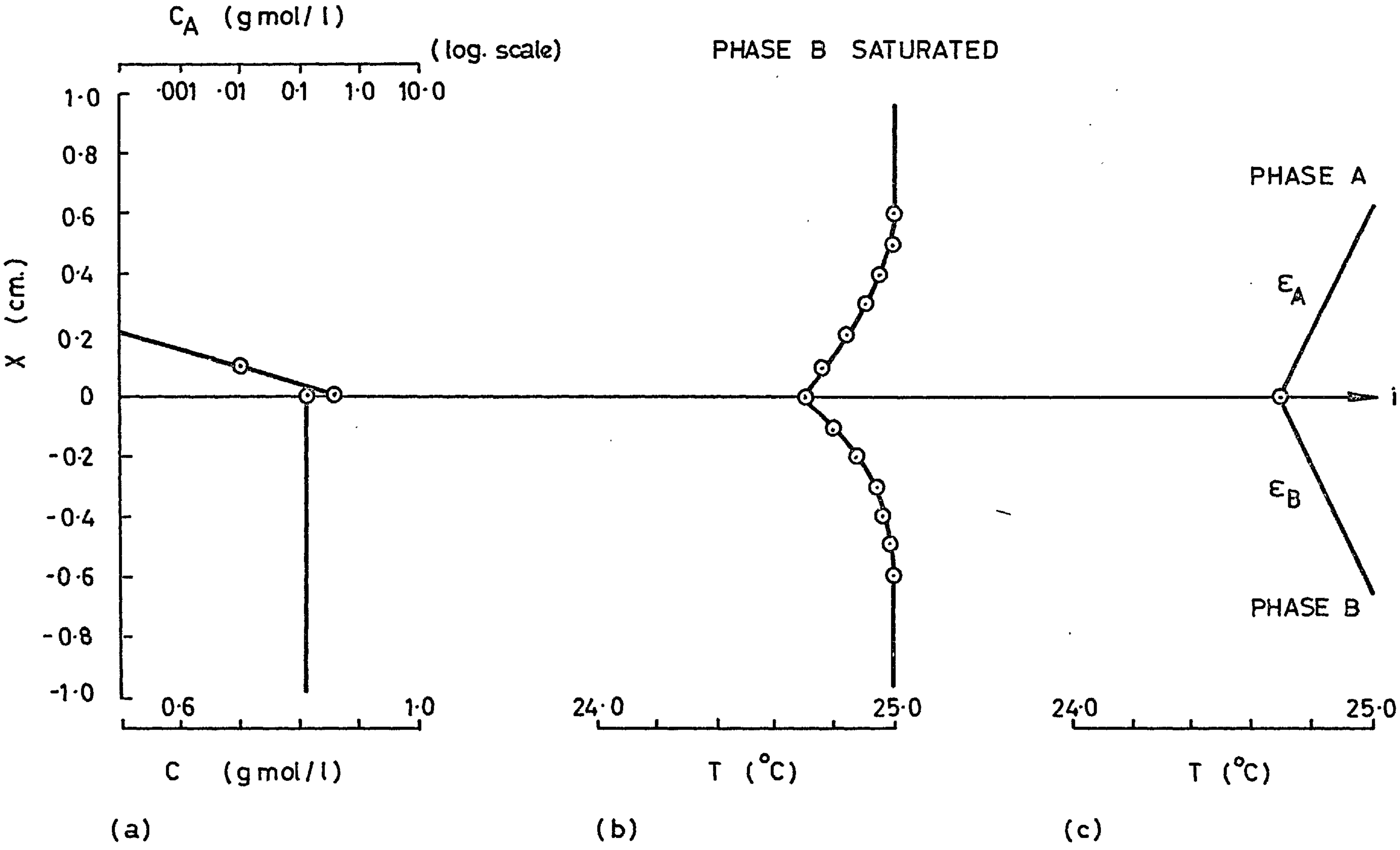


FIG. 5·24 CONCENTRATION AND TEMPERATURE PROFILES: HEXANE - ANILINE

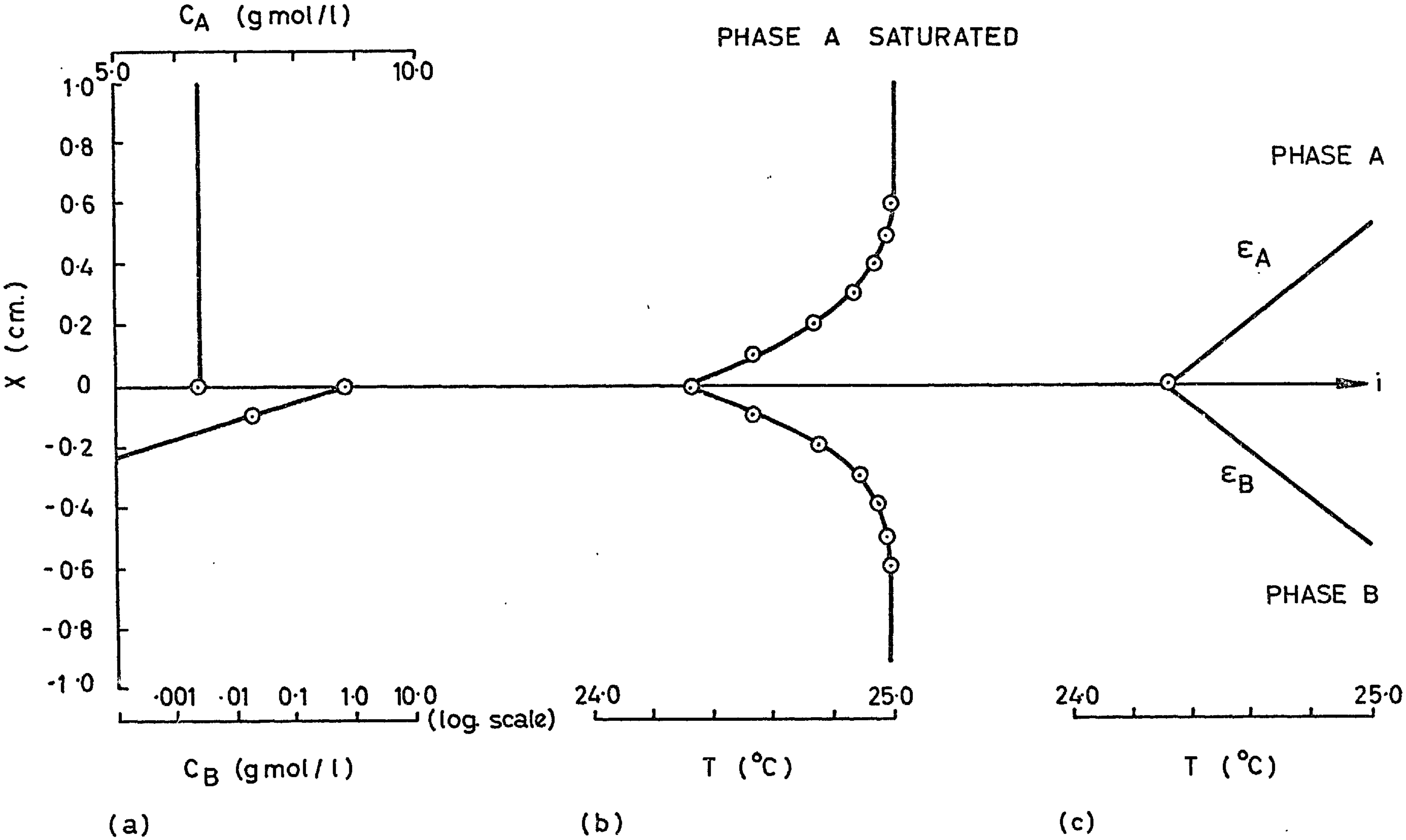


FIG. 5·25 CONCENTRATION AND TEMPERATURE PROFILES : HEXANE - ANILINE

5.4 Stability analysis

5.4.1 Qualitative analysis

According to the criteria of stability stationary instabilities may be expected when the sign of the temperature gradient and the rate of change of interfacial tension with temperature are the same and oscillatory instabilities may set in when mass transfer takes place out of the phase of higher viscosity. These two criteria are applied to the six selected systems in each direction of transfer. The results are summarized in table 5.5. Comparing the predicted stability with the experimental observations of Ying and Sawistowski(16) presented in table 5.1, agreement is found for the systems ethyl acetate-water and acetylacetone-water in both directions of transfer and for transfer of methyl ethyl ketone and cyclohexanol into water and aniline into hexane.

For the case of transfer of hexane into aniline and water into cyclohexanol, which are predicted stable contrary to the experimental observations, possible explanations are that transient effects could be responsible for the onset of stability or that there is an even number of values of γ_i for which the real part of equation 4.76 is equal to zero, as was discussed in section 4.8.2.

For the system isobutanol-water there is disagreement in both directions of transfer. The system has been reported unstable during the transfer of water into the organic phase under dynamic conditions.(13).

TABLE 5.5.

PREDICTION OF STABILITY BEHAVIOUR FOR SELECTED SYSTEMS

Liquid A	Liquid B	Direction of transfer	e^2	σ_T	ε_A	Stability predicted with respect to:-	
						Stationary dist.	oscillatory dist.
ethyl acetate	water	B→A	<1	−	+	stable	unstable
		A→B			−	unstable	stable
acetyl acetone	water	B→A	<1 (1)	−	+	stable	stable
		A→B			+	stable	unstable
isobutanol	water	B→A	>1	+	+	unstable	stable
		A→B			−	stable	unstable
methyl ethyl ketone	water	B→A	<1	+	+	unstable	unstable
		A→B			−	stable	stable
cyclohexanol	water	B→A	>>1	−	+	stable	stable
		A→B			−	unstable	unstable
hexane	aniline	B→A	<1	−	+	stable	unstable
		A→B			+	stable	stable

Since the variation of interfacial tension with temperature in this system is very small, as may be seen in figure 5.10, the system could be stable for a relatively wide range of wave lengths. In order to determine the instability curve of all the predicted unstable systems, the characteristic equation has to be solved to yield values of α and β at the onset of instability.

5.4.2 Numerical results

The characteristic equation was solved for stationary instability for the systems ethyl acetate-water, isobutanol-water, methyl ethyl ketone-water and cyclohexanol-water. Since only stationary instability is to be considered, the imaginery component of the growth constant, β_i, was made equal to zero. The calculations were done using the Imperial College CDC 6400 computer. The value of α_{NS} was obtained by making the value of β_r equal to zero in equation (4.6.2). Then, the values of β within the interval $\alpha = \alpha_{NS}$ to $\alpha = 0$ were calculated by trial and error.

A value DIF was defined as:

$$DIF = \alpha^2_G - \alpha^2_C \qquad (5.9)$$

where α_C is the value of α obtained from equation (4.62) for an arbitrary value of β_r and an assumed value of is denoted by α_G. Instead of solving the equation DIF $(\alpha, \beta_r) = 0$, which would have led to problems of multiplicity and a substantial amount of computation, a "chasing" method was adopted. The procedure consisted of computing equation (5.9) on a mesh of 300.000 points in the strip $\alpha = 0$ to $\alpha = \alpha_{NS}$, and instructing the computer to print only the values where a change of sign in two consecutive values DIF occurred.

In this way it was possible to determine a narrow band in which the curve DIF $(\alpha, \beta) = 0$ was contained in the interval $\alpha = 0$ to $\alpha = \alpha_{NS}$. From these values an iterative process was applied to refine the data already obtained until the pairs α, β satisfied equation (5.9) with an error smaller than one per cent.

The instability curves calculated with the linearised temperature profiles at a time equal to 30 seconds are shown in figures 5.26 to 5.29. The curves are similar to those determined by Sternling and Scriven$^{(8)}$ for concentration induced convective flows in ternary systems. The value of α_{NS} demarcates stable and unstable wave numbers. Since the systems remain stable for $\alpha > \alpha_{NS}$, the wave length of neutral stability is the minimum wave length for the onset of instability to be possible. Disturbances of larger size will grow and the smaller ones will be damped by the viscous shear forces opposing the motion at the interface. This explains why instabilities of small wave length grow least rapidly. The curves have a maximum corresponding to the size of the disturbance that grows most rapidly and ultimately dominates the system. The numerical results obtained for the dominant wave length, λ_D, the dominant growth constant, β_D, and the α_{NS} for the four studied systems are shown in table 5.6.

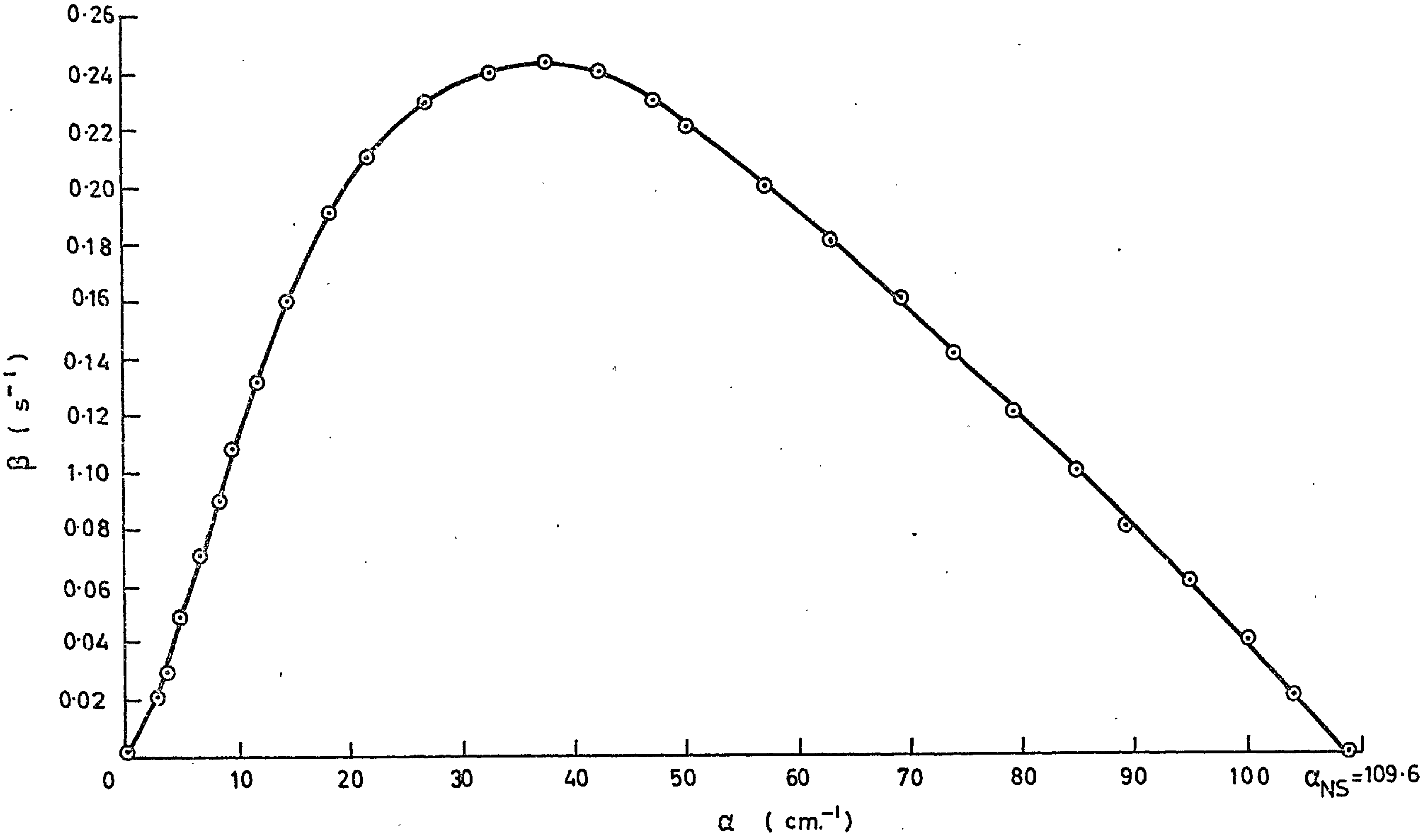


FIG. 5·26 GROWTH CONSTANT vs. WAVE NUMBER FOR TRANSFER OF ETHYL ACETATE INTO WATER

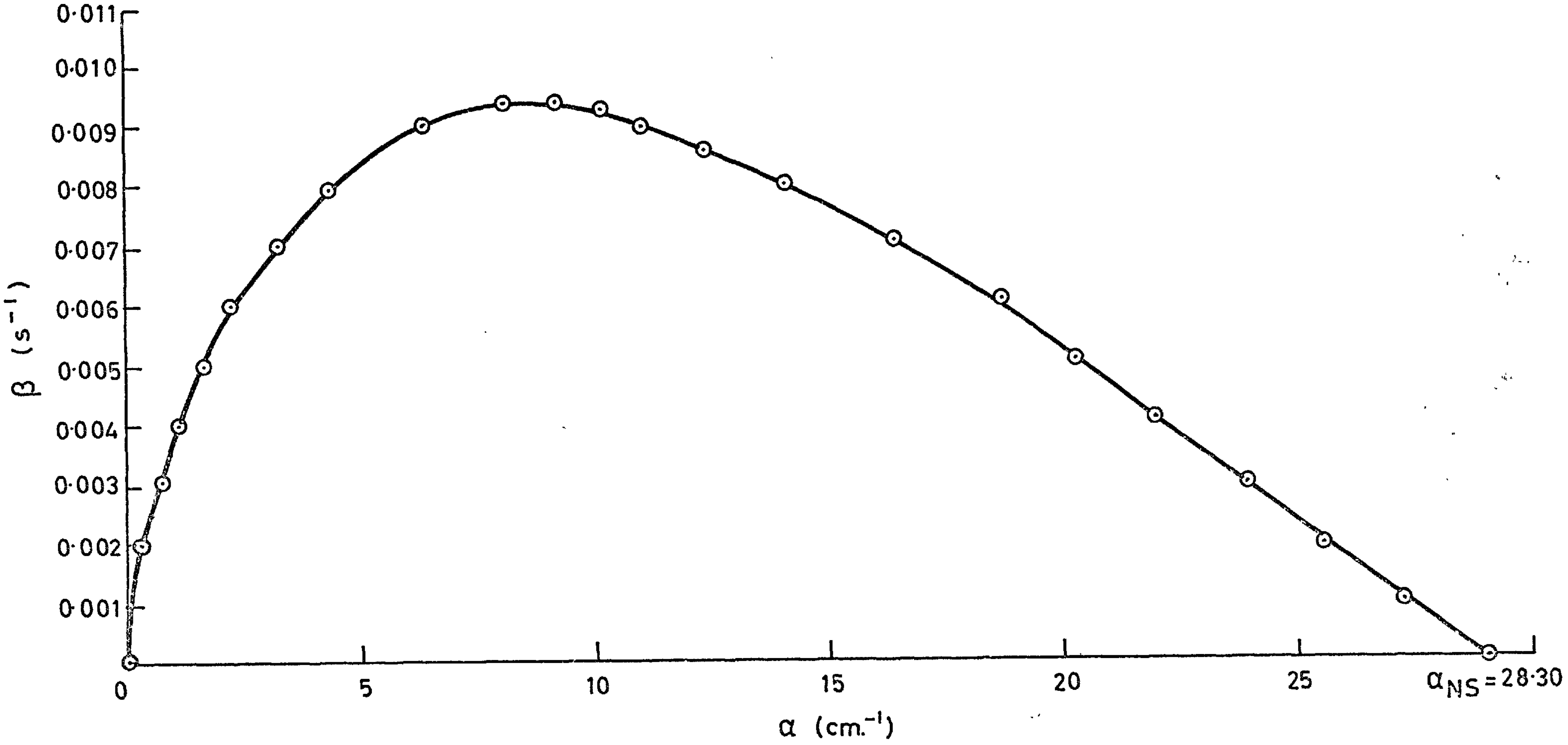


FIG. 5·27 GROWTH CONSTANT vs. WAVE NUMBER FOR TRANSFER OF WATER INTO ISOBUTANOL

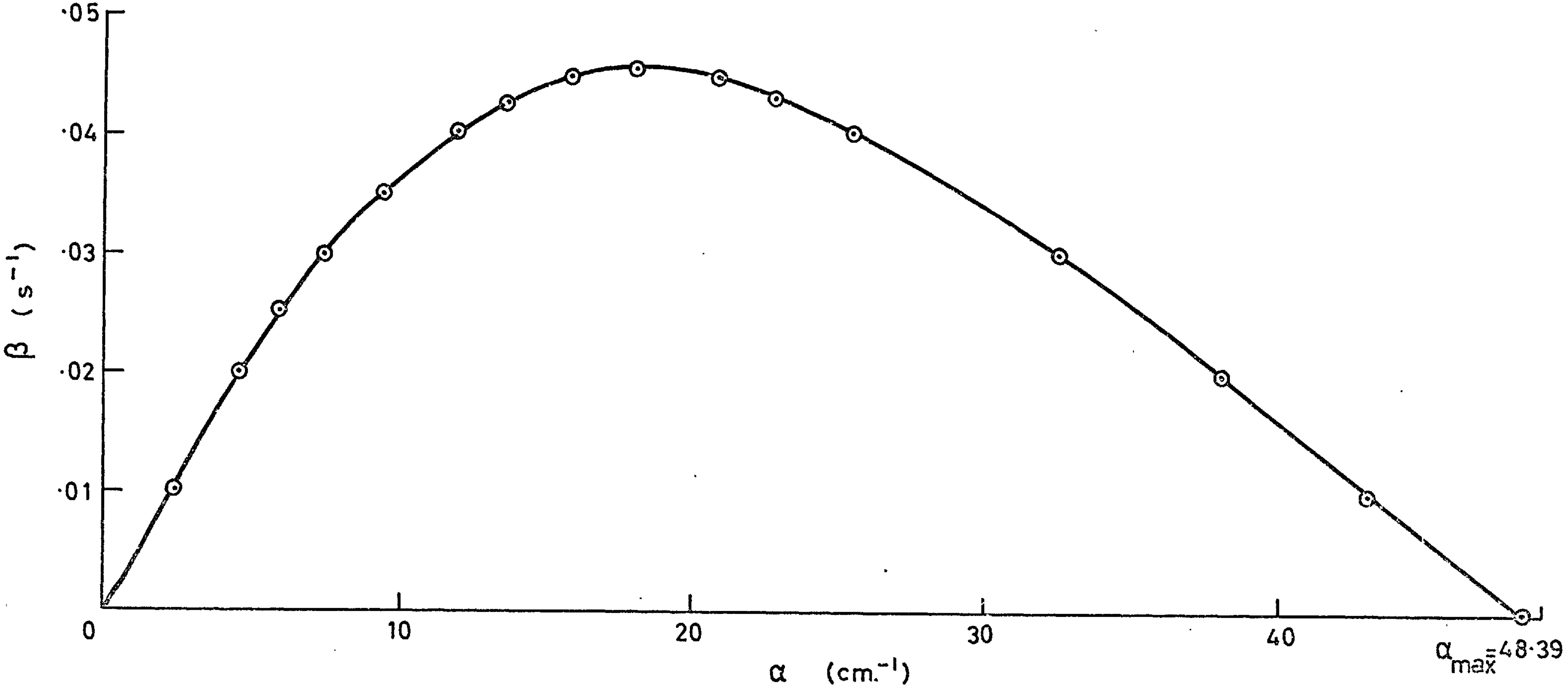


FIG. 5·28 GROWTH CONSTANT vs. WAVE NUMBER FOR TRANSFER OF WATER INTO METHYL ETHYL KETONE.

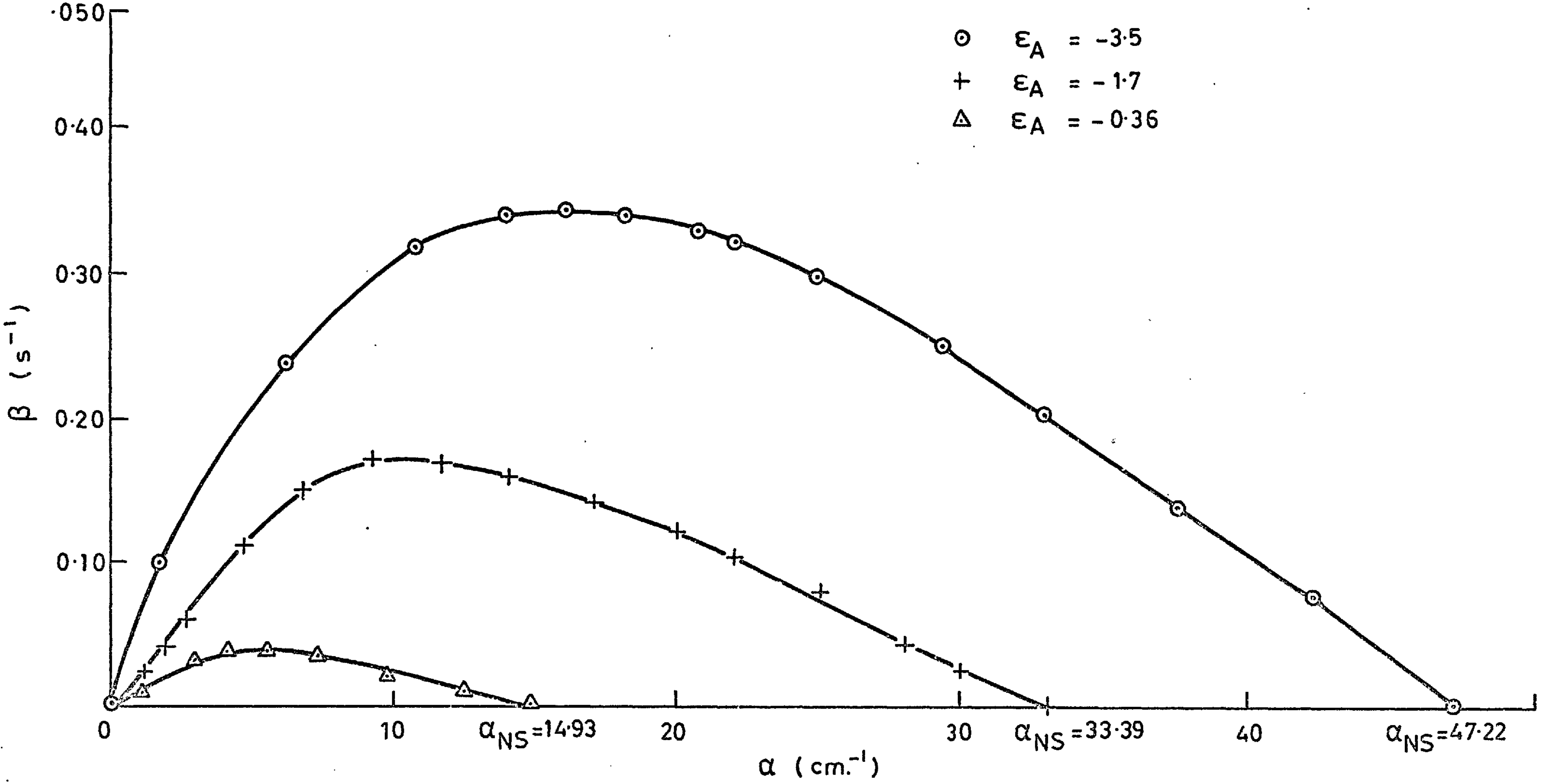


FIG. 5·29 GROWTH CONSTANT vs WAVE NUMBER FOR TRANSFER OF CYCLOHEXANOL INTO WATER AT DIFFERENT TEMPERATURE PROFILES

Since in the unstable systems instabilities set in a very short time after the phases are brought into contact$^{(16)}$ the instability curves were calculated at 5 and 15 seconds of contact for the system cyclohexanol-water. The object of this calculation was to investigate the dependence of the instability curve on the magnitude of the temperature profile, which is a function of time.

TABLE 5.6

RESULTS OF CALCULATIONS

Liquid B$^{(*)}$	Direction of transfer	λ_{NS} (cm)	λ_D (cm)	β_{rD} (s^{-1})
ethyl acetate	A→B	0.0621	0.167	0.222
isobutanol	B→A	0.214	0.74	0.0094
methyl ethyl ketone	B→A	0.130	0.349	0.0455
cyclohexanol	A→B	0.421	1.26	0.004

(*)Liquid A is water in all the systems.

The three instability curves are shown in figure 5.29 and the values of the corresponding temperature gradients, λ_{NS}, λ_D. λ_D are presented in table 5.7. For this system an increase of ten times the value of the temperature gradient, increased the growth in almost the same proportion and decreased the dominant wave length by three times.

TABLE 5.7

t	ε_A (°C/cm)	λ_{NS} (cm)	λ_D (cm)	β_{rD} (s^{-1})
5	-3.5	0.133	0.392	0.034
15	-1.7	0.188	0.628	0.017
30	-0.36	0.421	1.26	0.004

5.4.3 Discussion of results

The numerical results show that ethyl acetate-water is the most unstable system of the four analysed with respect to stationary instability since its α_{NS} is the lowest. This means that disturbances of wave length larger than 0.06 cm will be amplified. This is in good agreement with experimental results. In the other three systems much larger disturbances are required to induce instabilities. In the case of transfer of water into isobutanol, the maximum wave length of the disturbance for which the system still remains stable is about 4 times the wave length corresponding to the system ethyl acetate-water. This could explain the stable behaviour reported in experimental observations. The same argument applies to the system methyl ethyl ketone-water. The transfer of cyclohexanol into water is the most stable of the four unstable directions studied since it has the highest wave length of neutral instability. But this system is unstable with respect to oscillatory instabilities in the same direction of transfer. The oscillatory instability may be expected to be considerably strong since the ratio of viscosities in this system, e^2, if of the order of 40.

Comparing the experimentally established values of the densities of pure water and of water saturated with acetylacetone, table B.1 and B.3 respectively, it can be seen that there is a volume contraction on mixing. The density of the saturated solution is 1.0044 while the density of water is 0.9971. The increase in density near the interface creates a destabilising density gradient which in accordance with the work of Berg and Morig(12) will create density-driven convective instability. This behaviour, rather than oscillatory instabilities may explain the strong interfacial activity found experimentally in this system.

CHAPTER 6

CONCLUSIONS

The conclusions of this work can be summarised as follows:

1. Temperature effects accompanying mass transfer in binary liquid-liquid systems are of sufficient magnitude to produce Marangoni type instabilities.
2. The linearised analysis of stability shows that binary systems may be either stable or unstable in both directions of transfer.
3. The criteria of stability suggest that stationary instabilities are promoted by:
    a) positive heat of solution in systems with a negative change of interfacial tension with temperature.
    b) negative heat of solution in systems with positive change of interfacial tension with temperature.

    Oscillatory instabilities are most likely to occur for mass transfer out of the phase of higher viscosity.
4. Binary systems will be stable in both directions of transfer when the heat of solution and the change of interfacial tension with temperature have the same sign and the viscosities of the two phases are equal.
5. Predictions obtained from the stability criteria are in good agreement with experimental observations. Individual cases of lack of agreement can be explained in terms of size of perturbation.

Recommendations for future work

1. The numerical results were computed only for stationary instability for a set of systems. Further study of the effect of the magnitude of various parameters such as viscosity,ratio, ratio of thermal diffusivity, etc., would enable a more precise prediction to be obtained for the conditions at the onset of instability.
2. A similar analysis to that performed in the present work should be performed by for the oscillatory regime.
3. In order to allow for the effect of density-driven flows, the presence of density gradients should be incorporated in the model.
4. An attempt should be made to develop stability criteria for transient conditions of mass transfer.

APPENDIX A

LIMITING BEHAVIOUR OF THE CHARACTERISTIC EQUATION

A.1. Small values of γ

The six radicals in equations (4.62) and (4.75) have the form $= \sqrt{1 + x}$.

They can be expanded in binomial series of the form:

$$(1 - x)^{n} = 1 + nx + n(n-1)\ x^{2}/2! \ + \ldots \qquad \text{(A1)}$$

The series (A1) converges for $x \leqslant 1$ when $n > 0$. For small values of the variable the terms of second and higher order may be neglected. The expansion of p, q and g, equation (4.73) become:

$$\begin{aligned} q_A &= 1 + \gamma/2 & g_B &= 1 + h^{2}\gamma/2 \\ p_A &= 1 + j^{2}\gamma/2 & p_B &= 1 + j^{2}e^{2}\gamma/2 \qquad \text{(A2)} \\ q_A &= 1 + L_A\gamma/2 & q_B &= 1 + r^{2}L_A\gamma/2 \end{aligned}$$

The four terms in the numerator of equation (4.62) combined with expansions (A2) become:

$$\begin{aligned} (g_A+1)^{-1}(g_A+p_A)^{-1} &= 1/4 - \left[(2 + j^{2})\ \gamma + (1 + j^{2})\gamma/4 \right]/16 \\ (g_B+1)^{-1}(g_B+p_B)^{-1} &= 1/4 - \left[(2h^{2} + e^{2}j^{2})\ \gamma + h^{2}(h^{2}+e^{2}j^{2}\ \gamma 2/4 \right]/16 \\ (q_A+1)^{-1}(q_A+p_A)^{-1} &= 1/4 - \left[(2_{LA} + j^{2})\ \gamma + L_A\ (L_A + j^{2})\gamma 2/4 \right]/16 \\ (q_B+1)^{-1}(q_B+p_B)^{-1} &= 1/4 - \left[(2r^{2}L_A + e^{2}j^{2})\gamma + r^{2}L_A(r^{2}L_A+e^{2}j^{2})\gamma 2/4 \right]/16 \end{aligned} \qquad \text{(A3)}$$

Inserting equation (A3) into equation (4.62), the following expression for the numerator of equation (4.62) is obtained:

$$N_{M1} = \frac{1}{4}\left[1 - (1/sm) - E_A\ (\pounds_A - \pounds_B\ /\ \Omega^{o}{}_{C})\ /\varepsilon_A\right]$$

$$- \frac{1}{16}\left\{\left[2 + j^{2} - \left[(2h^{2} + e^{2}j^{2})/sm\right] - E_A\pounds_A\ (2L_A+j^{2})/\varepsilon_A + \right.\right.$$

$$+ E_A \pounds_B \; (2r^2 L_A + e^2 j^2) \; / \; \Omega^o{}_C \varepsilon_A \big] \big\} \gamma$$

$$- \frac{1}{16} \Big\{ (1 + j^2)/4 - \big[h^2 (h^2 + e^2 j^2)/4sm \big] - E_A \pounds_{A(L_A + j^2)/4\varepsilon_A}$$

$$+ E_A \; \pounds_B r^2 \; (r^2 L_A + e^2 j^2) \; /4\Omega^o{}_C \; \varepsilon_A \Big\} \gamma^2 \qquad \text{(A4)}$$

This equation has the form:

$$N_{M1} = a_{N1} + b_{NI}\gamma + C_{N1}\gamma^2 \qquad \text{(A5)}$$

Combining equations (A2) with equation (4.62), the denominator of equation (4.62) becomes,

$$D_{M1} = 2 \; Z_{20} \; Z_{30} + \Big\{ Z_{20} \; (1 + e^2 \mu_B/\mu_A) \; j^2$$

$$+ \big[E_A \; (R_A + R_B/\Omega^o{}_C) - 1 - 1/m \big] \; Z_{30} \Big\} \; \gamma$$

$$+ \big[E_A \; (R_A + R_B/\Omega^o{}_C) - 1 - 1/m \big] \; (1 + e^2 \mu_B/\mu_A) j^2 \; \gamma^2/4$$

(A6)

where:

$$Z_{20} = \big[\; E_A \; (R_A + R_B/\Omega^o{}_C \; h^2)/L_A \big] - 1 - 1/h^2 m$$

$$Z_{30} = 1 + (\mu_B/\mu_A) + \alpha_S/2_A$$

as defined in chapter 4.

Equation (A6) has the form:

$$D_{M1} = a_{D1} + b_{DI} \; \gamma + c_{DI} \; \gamma^2 \qquad \text{(A7)}$$

Expanding the inverse of equation (A6) for small values of γ:

$$D_{M1}{}^{-1} = 1 - a_{DI}{}^{-1} \; (b_{DI}\gamma + c_{DI}\gamma^2) \quad a_{DI}{}^{-1} \qquad \text{(A8)}$$

and multiplying equation (A5) by equation (A8), equation (4.62) is obtained for small values of γ:

$$M = \Big\{ a_{N1} - (b_{N1} + a_{N1} \; b_{D1})\gamma + \big[(b_{N1} \; b_{D1} - a_{N1} c_{D1})/a_{D1} - c_{N1} \big] \gamma^2$$

$$+ \; (c_{N1} \; b_{D1}/a_{DI} + b_{N1} c_{D1}/a_{D1}) \gamma^3 + (c_{N1} c_{D1}/a_{D1}) \gamma^4 \Big\} \; / \; a_{D1}$$

(A9)

Combining equations (A4), (A5), (A6) and (A7) with equation (A9) and neglecting the terms of higher order than one:

$$M = \left[\frac{1 - (1/sm) - (\pounds_A - \pounds_B/{Q^o}_C)\ E_A/\varepsilon_A}{8\ Z_{20}\ Z_{30}} \right] (1 - f\gamma) \qquad \text{(A10)}$$

where

$$f = \frac{1 - (h^2/sm) - (\pounds_A - \pounds_B r^2/{Q^o}_C)\ L_A E_A}{Z_4\ \varepsilon_A} + \\ + \frac{j^2\ \ 1 - (e^2/sm) - (\pounds_A - \pounds_B e^2/{Q^o}_C)\ \ E_A}{4\ Z_4\ \ \varepsilon_A} + \\ + \frac{E_A\ (R_A + R_B/{Q^o}_C) - 1 - 1/m}{2\ Z_{20}} + \\ + \frac{1 + (e^2\mu_B/\mu_A)\ j^2}{4\ Z_{30}} \qquad \text{(A11)}$$

where:

$$Z_4 = 1 - (1/sm) - (\pounds_A - \pounds_B/{Q^o}_C)\ E_A/\varepsilon_A,$$

as defined in chapter 4.

Equations (A10) and (A11) are equations (4.77) and (4.78) in chapter 4.

The first factor in equation (A10) is the dimensionless wave number of neutral stability represented by equation (4.63). Therefore, combining equation (A10) with equation (4.63):

$$M = M_{NS}\ (1 - f\gamma) \quad ; \quad \gamma \rightarrow 0 \qquad \text{(A12)}$$

On combining equations (4.65) and (4.66) with equation (A11), the expression for f for unidirectional mass transfer, equation (4.80), is obtained. The expressions of M for mass transfer in one direction only are obtained by substituting the corresponding expressions for M_{NS} and f into equation (A12).

A.2 Large values of γ

In this case it is again desirable to expand in series the six different radicals in equation (4.62). Since the binomial series (A1) converges for $x \leq 1$, it is convenient to write p, q and g in the following form:

$$g_A = \sqrt{\gamma}\sqrt{(1 + 1/\gamma)} \qquad g_B = h\sqrt{\gamma}\sqrt{1 + 1/h^2\gamma}$$

$$p_A = j\sqrt{\gamma}\sqrt{1 + 1/j^2\gamma} \qquad p_B = ej\sqrt{\gamma}\sqrt{1 + 1/j^2e^2\gamma}$$

$$q_A = \sqrt{L_A\gamma}\sqrt{1 + 1/L_A\gamma} \qquad q_B = r\sqrt{L_A\gamma}\sqrt{1 + 1/r^2 L_A\gamma}$$

(A13)

Expanding these expressions and neglecting terms of higher order than one:

$$g_A = \sqrt{\gamma}\,(1 + 1/2\gamma) \qquad g_B = h\sqrt{\gamma}\,(1 + 1/2h^2\gamma)$$

$$p_A = j\sqrt{\gamma}\,(1 + 1/2j^2\gamma) \qquad p_B = ej\sqrt{\gamma}\,(1 + 1/2j^2e^2\gamma)$$

$$q_A = \sqrt{L_A\gamma}\,(1 + 1/2\,L_A\gamma) \qquad q_B = r\sqrt{L_A\gamma}\,(1 + 1/2r^2L_A\gamma)$$

(A14)

Then:

$$(g_A+1)^{-1}(g_A+p_A)^{-1} = \frac{1-\gamma^{-1/2} - \left[(j+1)\gamma^{-1} + \gamma^{-3/2} + \gamma^{-2}/2\right]/2j}{(1+j)\gamma}$$

$$(g_B+1)^{-1}(g_B+p_B)^{-1} = \frac{1-(\gamma^{-1/2}/h - \left[(h+ej)\gamma^{-1} + \gamma^{-3/2} + \gamma^{-2}/2h)/2eh^2j\right.}{h(h+ej)^{\gamma}}$$

$$(q_A+1)^{-1}(q_A+p_A)^{-1} = \frac{1 - \gamma^{-1/2}/\sqrt{L_A}}{\sqrt{L_A}(j+\sqrt{L_A})\gamma} \qquad \text{(A15)}$$

$$- \frac{(\sqrt{L_A} + j)\gamma^{-1} + \gamma^{-3/2} + \gamma^{-2}/2\cdot\sqrt{L_A}}{2\,L_A\,j\,(j + \sqrt{L_A})\gamma}$$

$$(q_B+1)^{-1}(q_B+p_B)^{-1} = \frac{1 - \gamma^{-1/2}/r\sqrt{L_A}}{r\sqrt{L_A}\ (ej + r\sqrt{L_A})\gamma}$$

$$- \frac{(r\sqrt{L_A} + ej)\gamma^{-1} + \gamma^{-3/2} + \gamma^{-2}/2r\sqrt{L_A}}{2\ er^2\ L_A\ j\ (ej + r\sqrt{L_A})\ \gamma}$$

Combining these equations with equation (4.62) and neglecting terms of smaller order than $\gamma^{-3/2}$, the following expression for the numerator of equation (4.64) is obtained:

$$N_{M2} = \Big\{ 1/(1+j) - \big[1/smh(h+ej)\big] - E_A\mathcal{E}_A/\varepsilon_A \sqrt{L_A}\ (j + \sqrt{L_A})$$
$$+ E_A\mathcal{E}_B/\varepsilon_A Q^o{}_C\ r\ \sqrt{L_A}(ej + r\sqrt{L_A})\Big\}\ \gamma^{-1}$$
$$- \Big\{ 1/(1+j) - \big[1/smh^2(h+je)\big] + E_A\mathcal{E}_A/\varepsilon_A\sqrt{L_A}\ (j+\sqrt{L_A})$$
$$+ E_A\mathcal{E}_B/\varepsilon_A Q^o{}_C r^2 L_A\ (ej + r\sqrt{L_A})\Big\}\ \gamma^{-3/2} \tag{A16}$$

This equation has the form:

$$N_{M2} = a_{N2}\gamma^{-1} + b_{N2}\ \gamma^{-3/2} \tag{A17}$$

The expression for the denomination of equation (4.62) is:

$$D_{M2} = Z_6\ Z_7\ j\gamma + Z_6\ Z_{12}\ \gamma^{1/2}$$
$$Z_{11}\ Z_7\ j + Z_6\ Z_7\ j/2$$
$$Z_{11}\ Z_{12}\ \gamma^{-1/2} + Z_{11}\ Z_7\ j\gamma^{-1/2} \tag{A18}$$

where:

$Z_6 = \left[E_A \; (R_A + R_B / Q^{o}_{C} \; r) / \sqrt{L_A} \right] - 1 - 1/hm$, as defined in chapter 4.

$Z_7 = 1 + e \; \mu_B / \mu_A$, as defined in chapter 4.

(A19)

$Z_{11} = \left[E_A \; (R_A + R_B / Q^{o}_{C} \; r^3) / L_A^{3/2} \right] - 1 - 1/h^3 m$

$Z_{12} = 1 + (\mu_B / \mu_A) + \alpha \mu_S / \mu_A$

Equation (A18) has the form

$$D_{M2} = a_{D2} \; \gamma + b_{D2} \; \gamma^{1/2} + c_{D2} + d_{D2} \; \gamma^{-1/2} + w_{D2} \; \gamma^{-1} \qquad \text{(A20)}$$

The inverse of equation (A20) is, after making use of the adequate expansions:

$$\frac{1}{D_{M2}} = \frac{1 - (b_{D2} \; \gamma^{-1/2} + c_{D2} \; \gamma^{-1} + d_{D2} \; \gamma^{-3/2} + w_{D2} \; \gamma^{-2}) / a_{D2}}{a_{D2} \gamma} \qquad \text{(A21)}$$

Multiplying equation (A17) by equation (A21), combining the resulting expression with equations (A16) and (A18) and neglecting terms of smaller order than $\gamma^{-5/2}$, the equation for M for large values of γ is obtained:

$$M = \left[\frac{1 / (1 + j) - \left[1/smh \; (h + je) \right]}{Z_6 \; Z_7 \; j \; \sqrt{L_A} \; \varepsilon_A} \right.$$

$$\left. - \frac{\varepsilon_A / (j + \sqrt{L_A}) - \varepsilon_B / Q^{o}_{C} \; r \; (je + r \sqrt{L_A})}{Z_6 \; Z_7 \; j \; \sqrt{L_A} \; \varepsilon_A} \right] \gamma^{-2}$$

$$+ \left\{ \left[\frac{\left[(je + 1) / (j + 1) - (1/smh^2) \right] \mu_B}{Z_6 \; Z^2_7 \; j^2 \mu_A} \right. \right.$$

$$+ \frac{\left[\mathcal{E}_A \ (je + \sqrt{L_A}) \ / \ (j + \sqrt{L_A}) - \acute{\mathcal{E}}_B / \Omega^{o}{}_C \ r\right]}{Z_6 \ Z^2{}_7 \ j^2 \mu_A \ L_A \ \epsilon_A} \mu_B$$

$$+ \frac{1 - \left[(h + j) \ / \ \mathrm{smh}^2 \ (h + je)\right] - E_A \ (\mathcal{E}_A - \mathcal{E}_B \ / \ \Omega^{o}{}_C \ r^2) / \epsilon_A L_A}{Z_6 \ Z^2{}_7 \ j^2}$$

$$+ \frac{1/(1 + j) - \left[1/\mathrm{smh} \ (h + ej)\right]}{Z_6 \ Z^2{}_7 \ j^2 \ \mu_A} \alpha \mu_{\breve{S}}$$

$$- \left. \frac{\left[\mathcal{E}_A \ / \ (j + \sqrt{L_A})\right] - \mathcal{E}_B / \Omega^{o}{}_B \ r \ (je + r \sqrt{L_A})}{Z_6 \ Z^2{}_7 \ j^2 \ \epsilon_A \ L_A \ \mu_A} \ E_A \mu_S^{\alpha} \right] \Bigg\} \gamma^{-5/2} \qquad \text{(A22)}$$

Equation (A22) is equation (4.82) in chapter 4. The expressions of M for unidirectional transfer are obtained combining equation (A22) with equations (4.65) and (4.66).

TABLE B1

PHYSICAL PROPERTIES OF PURE LIQUIDS AT 25 °C

Liquid	ρ (g/l)	C_p (cal/g°C)	μ (cP)	ν x10^2 (cm^2/s)	K x 10^3 (cm^2/s)
ethyl acetate	0.8948(11)	0.478	0.432(11)	0.482	0.236
acetylacetone	0.9971(42)	0.54	0.726(42)	0.728	0.768
isobutanol	0.7978(11)	0.670	3.40(11)	4.270	0.697
methyl ethyl ketone	0.7995	0.549	0.3980	0.498	0.801
cyclohexanol	0.9418	0.41	38.	40.3	0.86
aniline	1.0165(11)	0.503	3.74(11)	3.685	0.81
hexane	0.6630(11)	0.527	0.329(11)	0.497	0.958
water	0.99707	0.99892	0.894	0.898	1.463

Unreferenced data obtained from standard physical data textbooks(38 - 41).

TABLE B2

PHYSICAL PROPERTIES OF SATURATED PHASE A(*) at 25 °C

System	ρ (g/l)	C_p (cal/ g°C)	μ (cP)	$\nu \times 10^2$ cm^2/sec	$K \times 10^3$ (cm^2/sec)	x_A
ethyl acetate-water	0.9012	0.551	0.474	0.526	0.410	0.140
acetylacetone-water	0.9732	0.65	0.7948	0.818	0.942	0.250
isobutanol-water	0.8324	0.820	3.20	3.98	1.046	0.456
methyl ethyl ketone-water	0.8325	0.684	0.5498	0.661	0.9996	0.300
cyclohexanol-water	0.9507	0.66	0.2257	0.237	0.111	0.416
hexane-aniline	0.6743	0.525	0.350	0.519	0.946	0.078

(*) Phase A is the organic phase in the organic liquid-water systems and the hexane phase in the system hexane-aniline.

TABLE B3

PHYSICAL PROPERTIES OF SATURATED PHASE B(*) AT 25 °C

System	ρ (g/l)	C_p (cal/g °C)	μ (cP)	$\nu \times 10^2$ cm^2/sec	$K \times 10^3$ (cm^2/sec)	x_B
ethyl acetate-water	0.9958	0.990	1.07	1.075	1.442	0.0164
acetylacetone-water	1.0044	0.98	1.184	1.178	1.442	0.0300
isobutanol-water	0.9849	0.992	1.27	1.29	1.447	0.0210
methyl ethyl ketone-water	0.9621	0.947	0.868	0.903	1.4167	0.070
cyclohexanol-water	0.9967	0.99	1.164	1.169	1.4588	0.007
hexane-aniline	0.9809	0.505	2.61	2.61	0.8220	0.081

(*) Phase B is the water phase in the organic liquid-water systems and the aniline phase in the system hexane-aniline.

TABLE B4

DIFFUSIVITIES AT 25 °C

Liquid A	Liquid B	D_Ax10^5 cm^2	D_Bx10^5 cm^2
ethyl acetate	water	3.31	0.93
acetylacetone	water	2.18	0.93
isobutanol	water	0.25	0.82
methyl ethyl ketone	water	5.25	1.09
cyclohexanol	water	0.728	0.89
hexane	aniline	2.73	3.60

TABLE B5

EQUILIBRIUM CONCENTRATION AND RATE OF CHANGE OF EQUILIBRIUM CONCENTRATION WITH TEMPERATURE

Phase A	Phase B	C^*_A (gmol/C)	C^*_B (gmol/l)	R_A (gmol/l °C)	R_B (gmol/l °C)
ethyl acetate	water	1.64	0.844	0.021	-0.008
acetyl acetone	water	1.71	1.66	-0.189	-0.026
isobutanol	water	7.8	1.064	0.035	-0.010
methyl ethyl ketone	water	4.5	3.0	0.014	0.028
cyclohexanol	water	6.0	0.37	0.031	-0.004
hexane	aniline	0.60	0.83	0.020	0.024

TABLE B6

INTERFACIAL TENSION MEASUREMENTS

System	T (°C)	wetted radius (cm)	drop vol. (ml)	$\rho_B - \rho_A$ (gr/l)	$r/v^{1/3}$	f	σ_o (dyn/cm)	σ_T (dyn/cm) °C
ethyl acetate-water	22	.331	0.0932	0.0931	0.733	0.605	6.74	
	25	.331	0.0909	0.0946	0.739	0.604	6.70	-0.03
	28	.331	0.0895	0.0957	0.741	0.604	6.68	
acetylacetone-water	22	.331	.201	0.0299	0.565	0.630	4.50	
	25	.331	.190	0.0312	0.579	0.628	4.46	-0.023
	28	.331	.177	0.0325	0.689	0.626	4.36	
isobutanol-water	22	0.101	0.00573	0.1516	0.560	0.632	2.15	
	25	0.101	0.00575	0.1525	0.559	0.632	2.17	0.005
	28	0.101	0.00574	0.1536	0.559	0.632	2.18	

TABLE B6 (continuation)

methyl ethyl ketone water	22	.101	0.00275	0.1259	0.713	0.602	0.90	
	25	.101	0.00294	0.1296	0.698	0.602	0.99	0.025
	28	.101	0.00303	0.1332	0.691	0.603	1.05	
cyclohexanol-water	22	0.331	0.108	0.0448	6.97	0.608	3.75	
	25	0.331	0.101	0.0460	7.12	0.606	3.67	-0.023
	28	0.331	0.977	0.0475	7.19	0.60	3.61	
hexane-aniline	22	0.101	0.003322	0.3106	0.678	0.612	2.56	
	25	0.101	0.00301	0.3066	0.692	0.603	2.39	-0.07
	28	0.101	0.00270	0.3025	0.720	0.602	2.12	

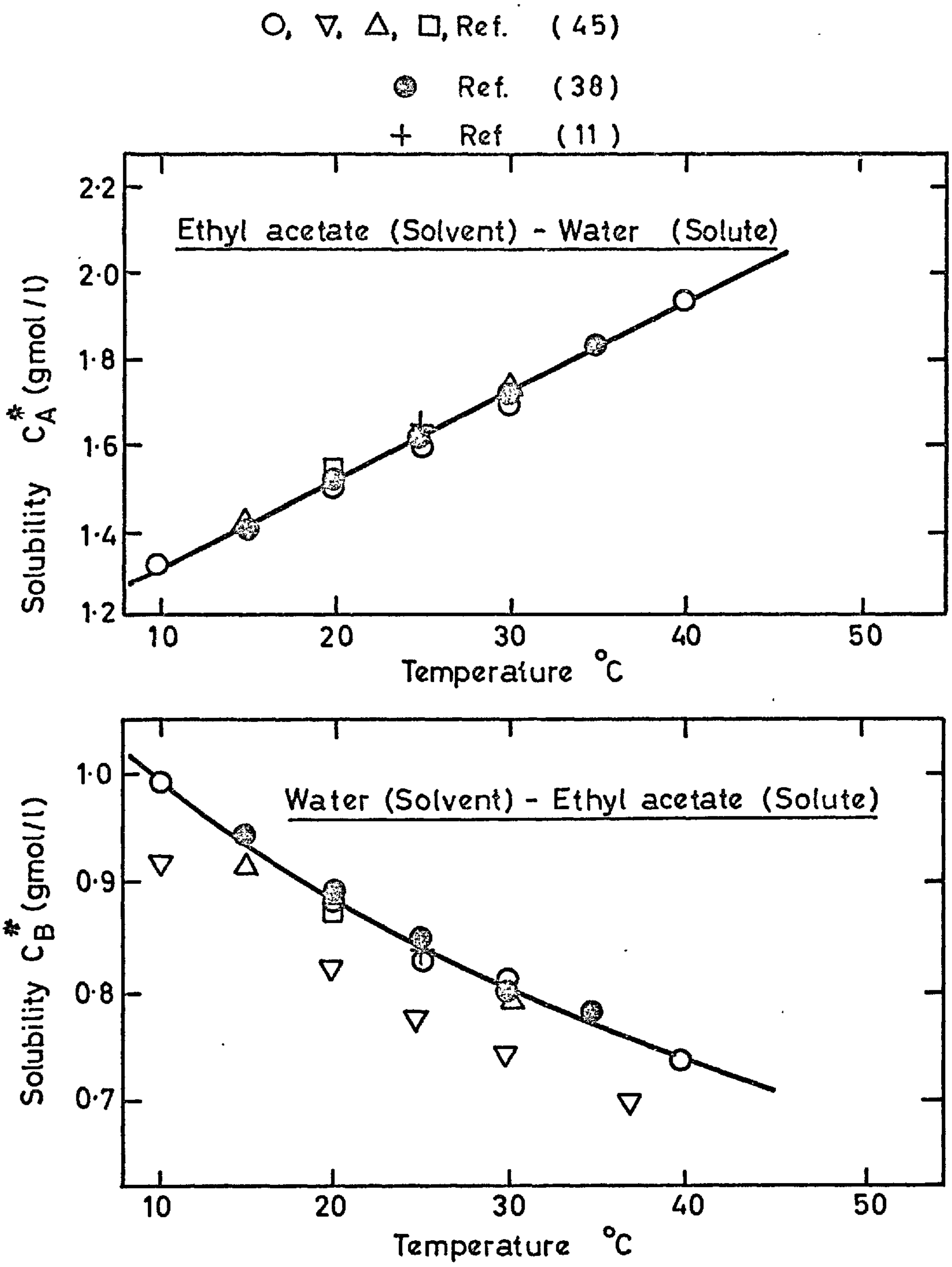


FIG. B1 MUTUAL SOLUBILITY, ETHYL ACETATE - WATER

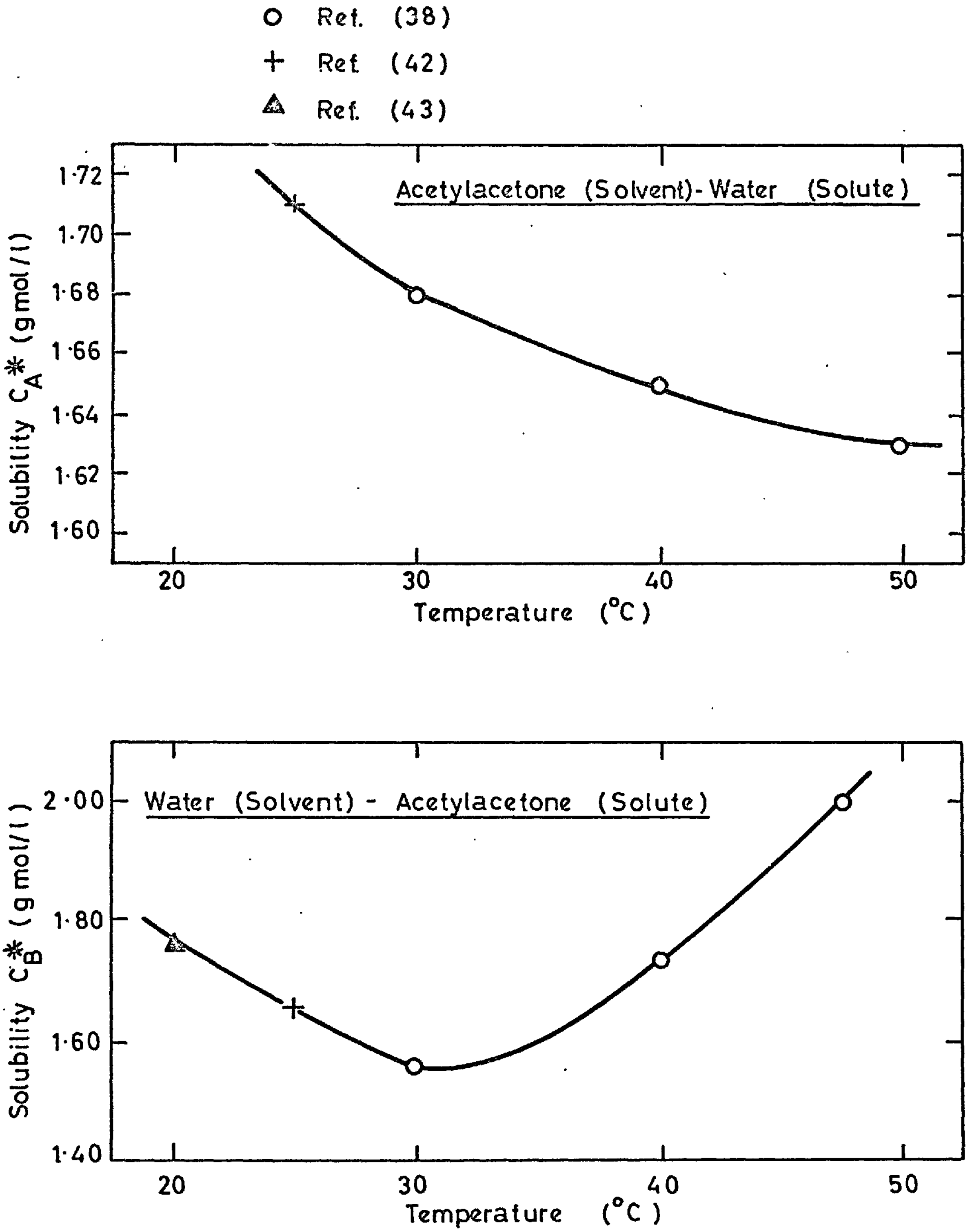


FIG. B.2 MUTUAL SOLUBILITY: ACETYLACETONE - WATER

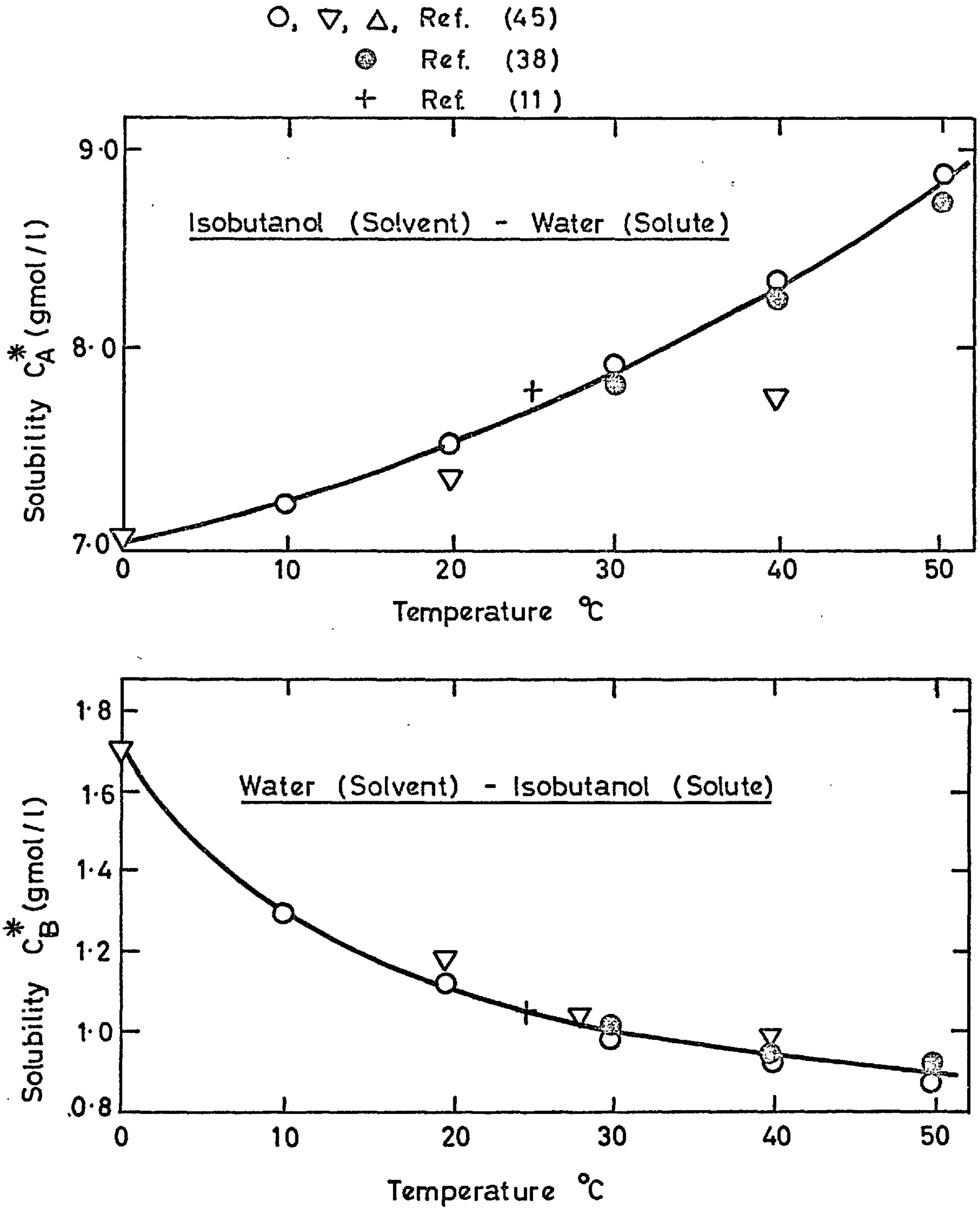


FIG. B3 MUTUAL SOLUBILITY, ISOBUTANOL-WATER

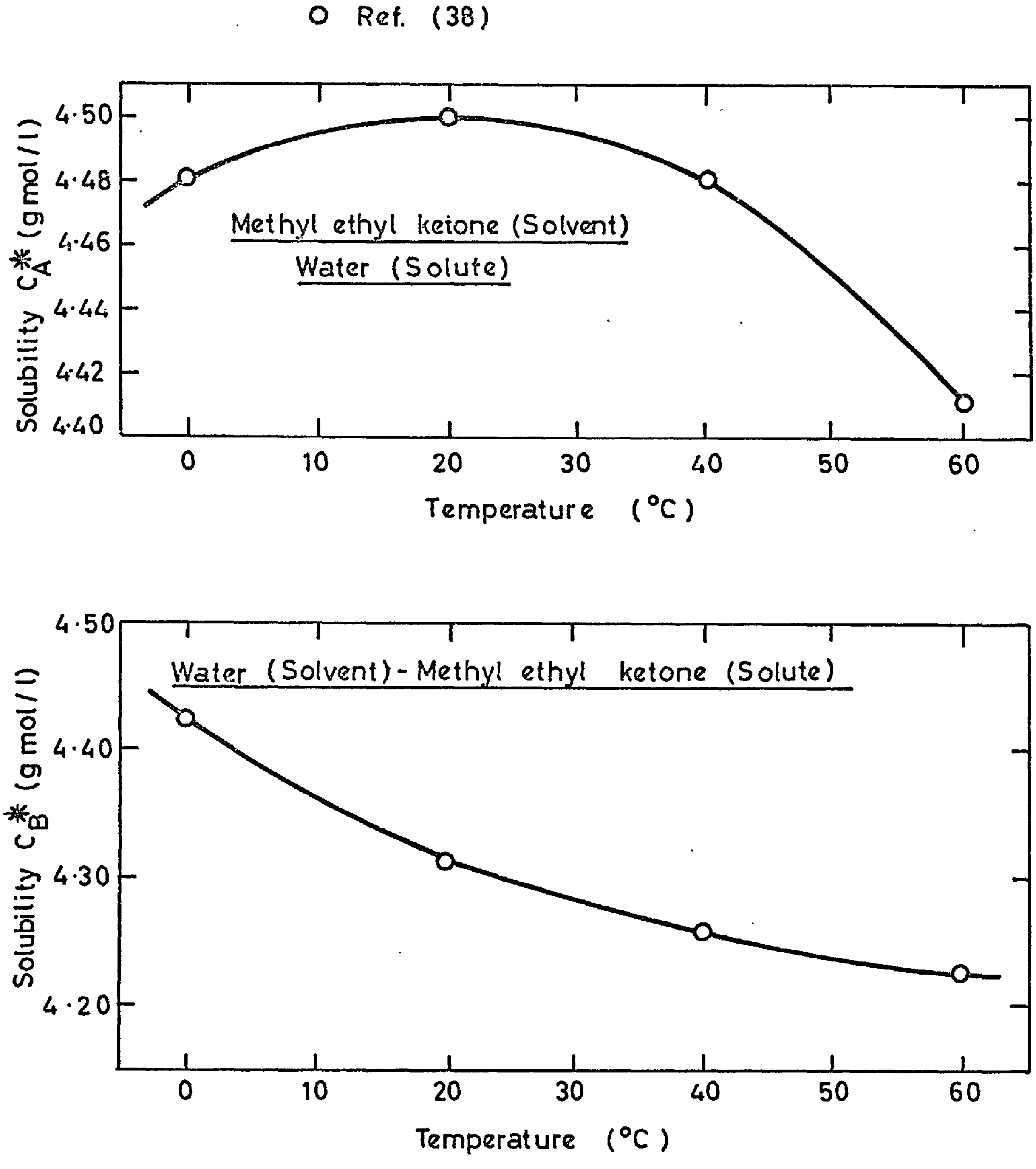


FIG. B.4 MUTUAL SOLUBILITY: METHYL ETHYL KETONE - WATER

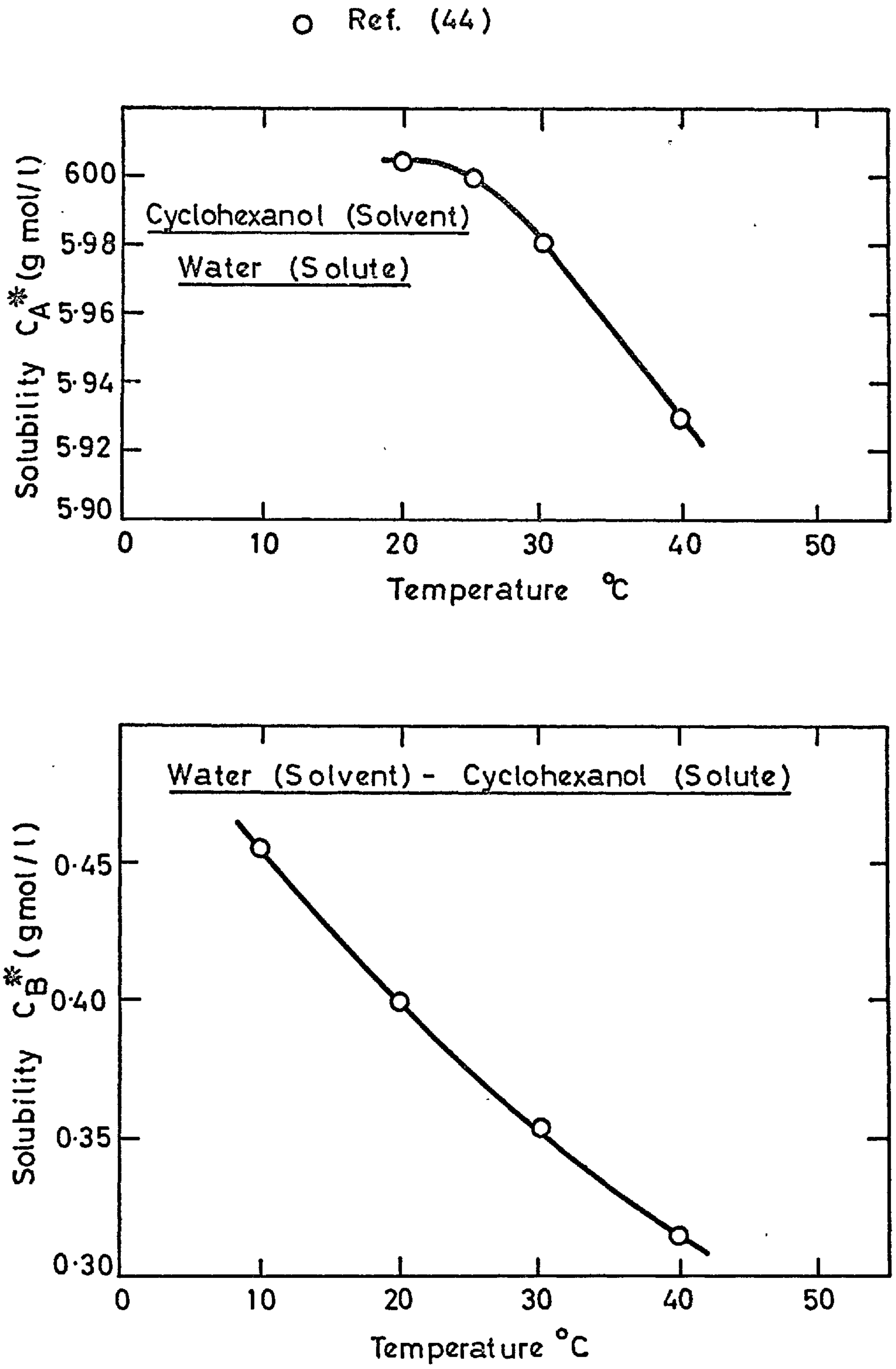


FIG. B.5 MUTUAL SOLUBILITY: CYCLOHEXANOL-WATER

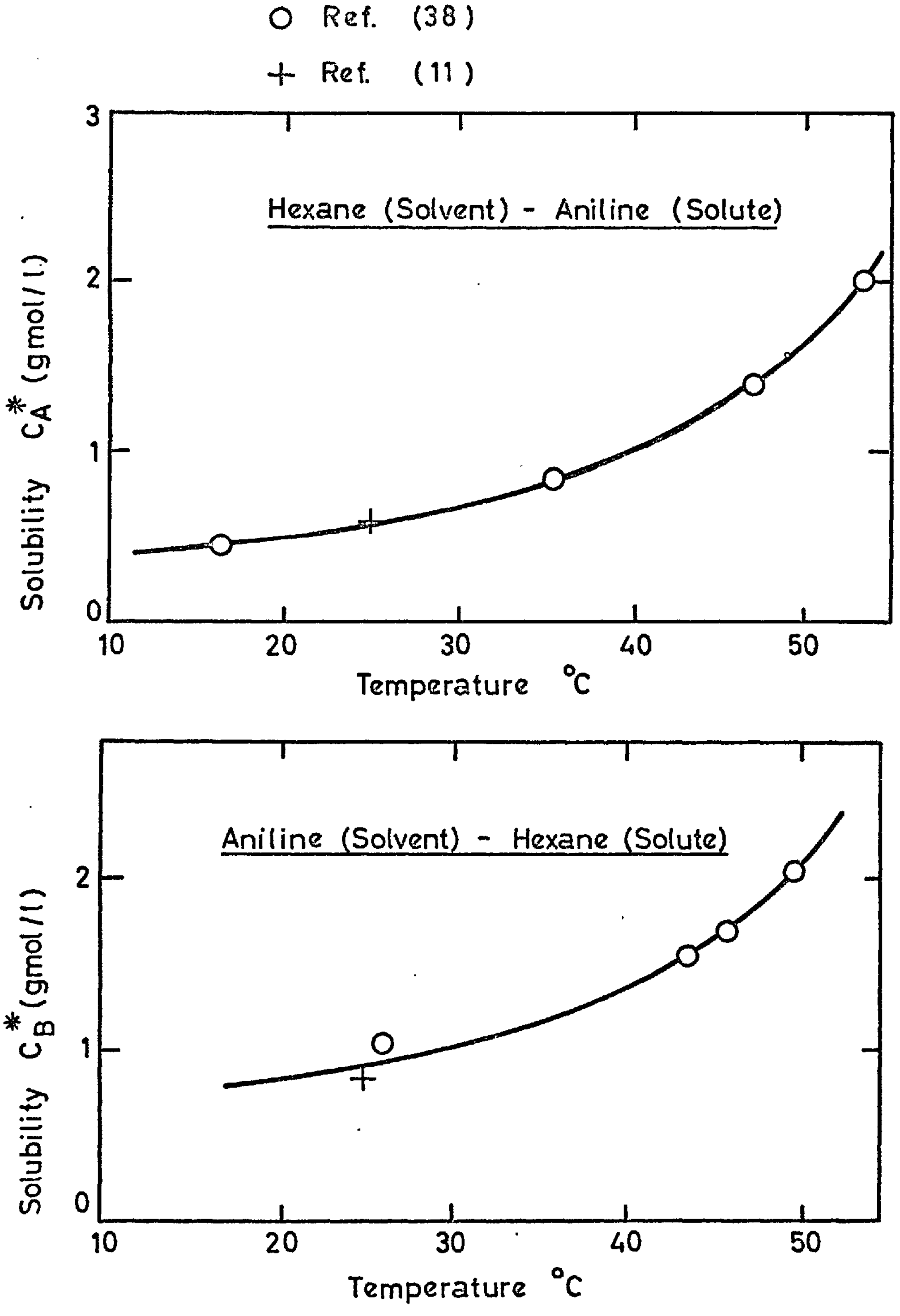


FIG. B6 MUTUAL SOLUBILITY, HEXANE - ANILINE

NOMENCLATURE

$A_{1,2}$	constants of integration
b	parameter defined by equation 4.80
B_1	constants of integration.
$C_{1,2}$	constants of integration.
C	concentration
c	wave velocity
C_p	heat capacity
d_t	penetration of temperature profile
D	mass diffusivity

$E = Q_r/MC_p$

$e = \sqrt{\nu_A/\nu_B}$

f = factor defined by equation 4.78.

$G = \mu\rho/\sigma_T\varepsilon_A$

$g = \sqrt{1 + \gamma}$

H = X part of the concentration perturbation.

$h = \sqrt{K_A/K_B}$

I = integral defined by equation 4.36

J = integral defined by equation 4.36

$j = \sqrt{K_A/\nu_A}$

K = thermal diffusivity

k = thermal conductivity

$L = K_A/D_A$

£ = undisturbed concentration profile

$l = i£/\alpha^2 D$

$\underline{M} = \mu_A K_A \alpha^2/\sigma_T \varepsilon_A$

M = molecular weight

$m = \rho_A C_{pA}/\rho_B C_{pB}$

$N_A = E_A R_A / L_A$

$N_B = E_B R_B / Q^o{}_c \; r^2 \; L_A$

P = X component of the temperature perturbation

$p = \sqrt{(1 + \beta/\alpha^2 \nu)}$

Q = heat of solution per mole of solution.

Q^o = heat of solution per mole of solute.

Q_T = total heat produced by heat of solution.

$Q^o{}_C = Q^o{}_A / Q^o{}_B$

$q = \sqrt{1 + \beta/\alpha^2 K}$

$R = dC^*/dT$

$R_c = R_A/R_B$

$r = \sqrt{D_A/D_B}$

T = temperature

Greek letters

α = wave number

β = growth constant

$\gamma = \beta/\alpha^2 \; K_A$

ε = unperturbed temperature profile

λ = wave length

μ = dynamic viscosity

μ_s = composite surface viscosity

ν = kinematic viscosity

ρ = density

σ_0 = equilibrium interfacial tension

$\sigma_T = \partial \sigma_o / \partial T$

τ_{XY} = component of the fluid sheer stress

φ = x part of the stream function

Ψ = stream function

Subscripts

A = phase A, $x > 0$
B = phase B, $x < 0$
D = dominant unstable disturbance
N = neutrally stable disturbance
O = oscillatory disturbance
S = stationary disturbance
i = imaginary part
r = real part

Superscripts

O = value in the undisturbed state
∇ = perturbation
primes = differentiation with respect to x.

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