Pergamon

Int. J. Heat Mass Transfer. Vol. 40, No. 3, pp. 545–555, 1997

0017–9310/97 $15.00+0.00

PII: S0017–9310(96)00125–1

Soret effects in ternary systems heated from below

J. P. LARRE
Laboratory of Mechanics, Paul Sabatier University, 118 road of Narbonne, 31062 Toulouse cedex, France

and

J. K. PLATTEN† and G. CHAVEPEYER
University of Mons-Hainaut, B-7000 Mons, Belgium

(*Received* 10 *November* 1995 *and in final form* 1 *April* 1996)

Abstract—We have investigated the stability of an horizontal liquid layer heated from below, in the Rayleigh–Bénard configuration, on a water–isopropanol–ethanol mixture. Neglecting the cross-diffusional effects, we have developed a linear stability analysis of the rest state and compared it with experiments. We did not find sufficient agreement. However, incorporating the cross-diffusion in the theory, it is possible to recover the critical parameters for the onset of convection. Copyright © 1996 Elsevier Science Ltd.

1. INTRODUCTION

Thermal convection in binary fluids has attracted a lot of researchers in the last 20 years. In the beginning of the seventies, attention was given to the linear stability theory in the Rayleigh–Bénard configuration. Let us recall here that a binary mixture, initially homogeneous in composition, submitted to a temperature gradient, will display at the steady state a concentration gradient due to the so-called thermal diffusion (or Soret) effect. Therefore, depending on the sign of the Soret coefficient, the onset of convection can be delayed or anticipated. To be more specific, let us consider a mixture of water–ethanol diluted in ethanol. In that case, ethanol migrates to the cold boundary, i.e. to the upper boundary in the Rayleigh–Bénard configuration. In other words, the denser component (water) migrates to the bottom of the container and therefore diminishes the adverse steady density gradient: convection is then delayed and the critical Rayleigh number increases. The opposite effect is sometimes observed, namely in concentrated solutions in alcohol, since the sign of the Soret coefficient is strongly dependent on composition of the system. Different teams have worked intensively on this problem before 1975 [1–6]. A review of these older studies may be found in the monograph by Platten and Legros [7]. In the last decade, a renewed interest was given to this problem, due to the rich dynamical behaviour involved in the case of a stabilizing concentration gradient (increase of the critical Rayleigh number): instability sets in as oscillations of increasing amplitude ('overstability' in contradistinction with the principle of 'exchange of stability' valid in a pure fluid), finite amplitude convection is characterized by travelling waves (TW), and sometimes by localized travelling waves (LTW), counter propagating travelling waves (CPTW), etc. Next, by increasing the Rayleigh number, there is a bifurcation towards steady overturning convection (SOC). In the late eighties, there has been an exponentially increasing number of publications on the subject, and it is hopeless to give an exhaustive list of them. Let us however quote some of the leading research teams which have contributed to a better knowledge of this subject: besides ourselves [8–12] we would like to mention the work directed by Lücke [13–18], Kolodner [19–23], Steinberg [24–26], and many others. Both theoretical work (linear as well as non-linear theory, e.g. amplitude equation or numerical simulations) and experimental work (e.g. shadowgraphy or very precise velocity field determinations by laser-doppler velocimetry, LDV) have been reported. Let us summarize here some of the main results that will be used subsequently in this paper.

The main parameter characterizing the binary mixture is the so-called separation ratio ψ defined as

$$\psi = \frac{D^{\mathrm{T}} N_1 N_2 \beta}{D\alpha} \tag{1}$$

where D is the isothermal diffusion coefficient, D^{T} the thermal diffusion coefficient, N_1N_2 the product of the mass fractions of the two components, α the thermal expansion coefficient and β the mass expansion coefficient since the density ρ is now written as

---

† Author to whom correspondence should be addressed.

NOMENCLATURE

C_P	specific heat
D	isothermal diffusion coefficient
D^n	nth derivative with respect to z
D^T	thermal diffusion coefficient
d	depth of the layer
k	wave number
g	gravitional acceleration
J	mass flux
N	mass fraction
Pr	Prandtl number
r	reduced Rayleigh number
Ra	Rayleigh number
Sc	Schmidt number
T	temperature
t	time
v	velocity
W	thermal flux
X	generalized force
x, y	horizontal coordinates
z	vertical coordinate.

Greek symbols

α	thermal expansion coefficient
β	mass expansion coefficient
ΔT	temperature difference
κ	thermal diffusivity
λ	thermal conductivity
μ_i	chemical potential of component i
ν	kinematic viscosity
Π	period
ρ	density
Φ	stream function
ψ	separation factor
ω	critical frequency.

Subscripts

cold	cold limit
crit	critical
hot	hot limit
ij	component i, j
TW	travelling wave
ter	ternary
x	horizontal
y	horizontal
z	vertical
0	reference state.

Superscripts

ex	exchange of stability
over	overstability
S	steady-state
0	reference state.

$$\rho = \rho_0[1-\alpha(T-T_0)+\beta(N_1-N_1^0)]. \qquad (2)$$

Since from non-equilibrium thermodynamics the sign of the cross-coefficient in the phenomenological fluxes is not prescribed, D^T may be positive or negative, depending on the sense of migration of the solute, thus the sign of ψ is not fixed. The critical Rayleigh number, deduced from the linear stability theory reads (in the case of free, permeable and conductive boundaries)

$$Ra^{ex} = Ra^0\left(1+\psi\frac{Pr+Sc}{Pr}\right)^{-1} \qquad (3)$$

$$Ra^{over} = Ra^0\frac{(1+Sc)(Pr+Sc)}{Sc^2}\left(1+\psi\frac{Pr}{(Pr+1)}\right)^{-1}, \qquad (4)$$

where Ra^{ex} is the critical Rayleigh number in the case of exchange of stability, Ra^{over} is the critical Rayleigh number in the case of overstability, Pr is the Prandtl number ($Pr = \nu/\kappa$, ν the kinematic viscosity and κ the thermal diffusivity), Sc is the Schmidt number ($Sc = \nu/D$), $Ra^0 = 27\pi^4/4$ is the critical Rayleigh number for a pure fluid ($\psi = 0$), with the same boundary conditions. When $\psi < 0$, the critical Rayleigh number is greater than Ra^0, and moreover $Ra^{over} < Ra^{ex}$ provided that

$$\psi < -\frac{Pr(Pr+1)}{(1+Sc)(Sc+Pr)+Pr^2}. \qquad (5)$$

If $Sc \gg Pr$, which is usually the case in most of liquid systems, like water–alcohol solutions ($Pr \approx 10$, $Sc \approx 1000$), the condition (5) becomes $\psi < -10^{-4}$, which is usually fulfilled since $\psi \approx -10^{-1}$. Therefore we conclude that when the concentration gradient is stabilizing, overstability prevails and the linear theory provides also the critical frequency at onset of convection

$$\omega = \frac{3\pi^2}{2}(Pr)\sqrt{\frac{-\psi(Sc+Pr)(Sc+1)}{PrSc^2(1+Pr+\psi Pr)}-\frac{1}{Sc^2}}. \qquad (6)$$

The Prandtl number, written in the above equation between parentheses in front of the square root sign, has to be omitted when the time scale used is d^2/ν instead of d^2/κ.

Equations (3)–(6) are valid without restriction for free, permeable and conductive boundary conditions. However approximate formulas may be obtained when $Sc \gg Pr$, and these formulas can be extended, at least approximately, to the more realistic case of rigid, impermeable and conductive conditions

$$r = \frac{Ra^{over}}{Ra^0} \approx 1-\frac{b\psi}{1+1/Pr+\psi} \qquad (7)$$

$$\omega \approx a\frac{3\pi^2}{2}\left(\frac{1}{Pr}\right)\sqrt{\frac{-\psi}{1+1/Pr+\psi}}. \qquad (8)$$

Note that $(1/Pr)$ in front of the square root sign in equation (8) has to be omitted when the time scale is d^2/κ instead of d^2/ν. In equations (7) and (8), the two constants a and b are [5, 22]:

(1) $a = 1$; $b = 1$ for free, permeable and conductive boundaries, i.e. $Ra^0 = 27\pi^4/4$;

(2) $a = 1.43$; $b = 1.05$ for rigid, impermeable and conductive boundaries, i.e. $Ra^0 = 1708$.

Near room temperature many experiments were done on water–alcohol solutions, in particular on water–ethanol and water–isopropanol solutions. The two sets of experiments on the two systems allow the determination of the two separation ratios ψ_1 and ψ_2 together with the two frequencies ω_1 and ω_2. A complete agreement was found with the linear theory.

The question now arises to know what happens in the ternary system water–ethanol–isopropanol initially homogeneous and heated from below. Do the two separate stabilizing effects mutually reinforce themselves? At what frequency does the system oscillate, close to ω_1 or close to ω_2? Can we find a relation between the frequency of oscillation ω_{ter} in a ternary system and the two frequencies ω_1 and ω_2 in the two separate binary solutions? This is the object of this paper. Thus we decided to reconsider the linear stability theory, to extend it to ternary systems, and to perform new experiments on ternary systems.

Besides its fundamental interest, this problem may have some industrial applications, e.g. in the oil industry, since one usually has to face polynary systems (like a mixture of many hydrocarbons).

To close the introduction, let us mention that triply diffusive fluid layer in the Rayleigh–Bénard configuration have already been studied in the past (theoretical study of the onset of convection) [27–30]. However it was clearly stated in all those papers that 'Soret, Dufour, and other off-diagonal contributions to the fluxes of the stratifying agencies are neglected'. The main objective of the above mentioned papers is thus totally different from ours: here we start with an homogeneous liquid layer, and the stratification is induced by the 'off-diagonal contributions', namely by Soret effects. Moreover, we have in mind an experimental study, not a topological study of the neutral curves.

2. PHENOMENOLOGICAL FORMS OF THE FLUXES

In ternary systems submitted to a temperature gradient, there are three mass fluxes: J_i ($i = 1, 2, 3$) and one thermal flux W, related to the thermodynamic generalized forces $X_i = -\text{grad}(\mu_i)_T$ (μ_i is the chemical potential of component i, $i = 1, 2, 3$) and $X_{\text{th}} = -\text{grad}(T)/T$ by linear laws

$$\begin{aligned} J_1 &= a_{11}X_1 + a_{12}X_2 + a_{13}X_3 + a_{1\text{th}}X_{\text{th}} \\ J_2 &= a_{21}X_1 + a_{22}X_2 + a_{23}X_3 + a_{2\text{th}}X_{\text{th}} \\ J_3 &= a_{31}X_1 + a_{32}X_2 + a_{33}X_3 + a_{3\text{th}}X_{\text{th}} \\ W &= a_{\text{th}1}X_1 + a_{\text{th}2}X_2 + a_{\text{th}3}X_3 + a_{\text{thth}}X_{\text{th}}. \end{aligned} \qquad (9)$$

Among the 16 coefficients a_{ij}, there exist 10 relations: the sum of the three mass fluxes must be equal to zero (four conditions) and six Onsager reciprocal relations.

Thus there are three independent fluxes related to the forces by six phenomenological coefficients.

$$\begin{aligned} J_1 &= a_{11}(X_1 - X_3) + a_{12}(X_2 - X_3) + a_{1\text{th}}X_{\text{th}} \\ J_2 &= a_{12}(X_1 - X_3) + a_{22}(X_2 - X_3) + a_{2\text{th}}X_{\text{th}} \\ W &= a_{1\text{th}}(X_1 - X_3) + a_{2\text{th}}(X_2 - X_3) + a_{\text{thth}}X_{\text{th}}. \end{aligned} \qquad (10)$$

Among these six coefficients, three are related to isothermal diffusion (a_{11}, a_{22} and a_{12}), two coefficients ($a_{1\text{th}}$ and $a_{2\text{th}}$) are related to the two thermal diffusion effects and one coefficient (a_{thth}) to the thermal conductivity of the mixture.

Equations (10) show that the thermodynamic forces are $(X_1 - X_3)$, $(X_2 - X_3)$ and X_{th}. However we would like to keep mass fraction gradients as the forces. Since the three gradients of chemical potential $X_i = -\text{grad}(\mu_i)_T$ ($i = 1, 2, 3$) are connected by the Gibbs–Duhem equation, it is possible to eliminate say $X_3 = -\text{grad}(\mu_3)_T$ in the above equations (10) and next to introduce the gradients of mass fractions by:

$$\text{grad}(\mu_1)_T = \left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,N_2} \text{grad}(N_1) + \left(\frac{\partial \mu_1}{\partial N_2}\right)_{T,N_1} \text{grad}(N_2) \qquad (11)$$

and a similar expression for $\text{grad}(\mu_2)_T$.

In this way we get

$$\begin{aligned} J_1 &= -\rho D_{11}\text{grad}(N_1) - \rho D_{12}\text{grad}(N_2) - \frac{a_{1\text{th}}}{T}\text{grad}(T) \\ J_2 &= -\rho D_{21}\text{grad}(N_1) - \rho D_{22}\text{grad}(N_2) - \frac{a_{2\text{th}}}{T}\text{grad}(T) \\ W &= -\rho D_{\text{F}1}\text{grad}(N_1) - \rho D_{\text{F}2}\text{grad}(N_2) - \frac{a_{\text{thth}}}{T}\text{grad}(T). \end{aligned} \qquad (12)$$

Clearly the four isothermal diffusion coefficients D_{ij} are nothing else than abbreviations for long quantities containing the Onsager coefficients a_{ij}, the partial derivatives of the chemical potentials $(\partial\mu_i/\partial N_j)$ and the mass fractions N_i of the three components. These four coefficients D_{ij} are not independent since there are only three independent Onsager coefficients a_{11},

a_{12}, a_{22}, and a formal linear relation could be obtained expressing e.g. D_{21} in terms of D_{11}, D_{12}, D_{22} and also in terms of $(\partial\mu_i/\partial N_j)$ and N_i. However this relationship will not be derived here, since we will not use it further. Of course, equations (12) are very general and could be written down immediately without any thermodynamical justification. Equations (12) also introduce two Dufour coefficients, D_{F1} and D_{F2}, but as usual in liquids, the Dufour effect will be neglected in the subsequent paragraphs.

The form of the phenomenological fluxes (12) closely resembles that obtained by the kinetic theory of gases [31]. However, for gases the diffusion coefficients are simply related to the mass and sizes of the molecular species. In particular for a ternary mixture of rigid spheres of equal size and mass it can be shown that the cross-diffusion coefficients D_{12} and D_{21} are identically zero.

We will work out the theory neglecting in a first step cross-diffusional effects, even if the solute molecule 'ethanol' and 'isopropanol' used in the experimental part are not of equal mass and size, and certainly not rigid spheres, hoping that our approximations will reflect the experiments, since finally the mass and size of the two solutes are not too different.

There are other justifications for neglecting cross-diffusion. Indeed, since our goal is the study of two simultaneous thermal diffusion effects, we may not introduce at the same time in the equations a supplementary effect, namely cross-diffusion, which is an isothermal effect. The study of cross-diffusion in isothermal systems with two imposed solute gradients, has been worked out by McDougall [32]. Last, but not least, the values of cross-diffusion coefficients are generally not known, and we feel not worth, for the time being, introducing into equations cross-diffusion coefficients whose signs are even not known.

Finally let us write

$$\frac{a_{\text{thth}}}{T} = \lambda$$

$$\frac{a_{1\text{th}}}{T} = \rho(D^{\text{T}}_{12}N_1N_2 + D^{\text{T}}_{13}N_1N_3)$$

$$\frac{a_{2\text{th}}}{T} = \rho(-D^{\text{T}}_{12}N_1N_2 + D^{\text{T}}_{23}N_2N_3). \qquad (13)$$

The reason for introducing new phenomenological coefficients D^{T}_{ij}, is to recover formally the expressions which are employed in all the three conceivable binary mixtures. We also hope that the D^{T}_{ij} are less concentration dependent than the $a_{i\text{th}}$.

With all our assumptions, the new forms of the phenomenological laws are:

$$\begin{aligned} J_1 &= -\rho D_{11}\text{grad}(N_1) - \rho(D^{\text{T}}_{12}N_1N_2 \\ &\quad + D^{\text{T}}_{13}N_1N_3)\text{grad}(T) \\ J_2 &= -\rho D_{22}\text{grad}(N_2) - \rho(-D^{\text{T}}_{12}N_1N_2 \\ &\quad + D^{\text{T}}_{23}N_2N_3)\text{grad}(T) \\ W &= -\lambda\text{grad}(T). \end{aligned} \qquad (14)$$

Since we have in mind experiments in *dilute* solutions of ethanol and isopropanol in water (the solvent), it is quite natural to consider the two independent fluxes J_1 and J_2 as being those of the two solutes (component 3 in water, component 1 will be isopropanol and 2 ethanol). Moreover since $N_1 \ll 1$ and $N_2 \ll 1$, the product N_1N_2 will be neglected and the final phenomenological laws that we will use in the linear stability analysis are

$$\begin{aligned} J_1 &= -\rho D_{11}\text{grad}(N_1) - \rho D^{\text{T}}_{13}N_1N_3\text{grad}(T) \\ J_2 &= -\rho D_{22}\text{grad}(N_2) - \rho D^{\text{T}}_{23}N_2N_3\text{grad}(T) \\ W &= -\lambda\text{grad}(T). \end{aligned} \qquad (15)$$

Thus, we are not really studying a ternary mixture, but more precisely two binary mixtures (of 1 and 3, and of 2 and 3) present simultaneously in the cell without interaction, each of these binary mixtures contributing separately to the density gradient, and therefore to the stability of the system.

Attention should be given to the fact that, in binary mixtures, the independent flux was conventionally taken as that of the denser component (i.e. in the present case water, the solvent); thus there will be a change of sign in the values of D^{T}_{ij}, but also of the mass expansion coefficient β_i, which will not affect the sign of the separation ratios ψ_i, of the two solutes.

3. THE LINEAR STABILITY ANALYSIS

We assume the following equation of state (16), where α is the thermal expansion coefficient, β_1 and β_2 the mass expansion coefficients of the two solutes:

$$\rho = \rho_0[1 - \alpha(T - T_0) + \beta_1(N_1 - N^0_1) + \beta_2(N_2 - N^0_2)]. \qquad (16)$$

The two-dimensional conservation equations (Fig. 1), using the so-called Boussinesq hypothesis, are

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} = 0$$

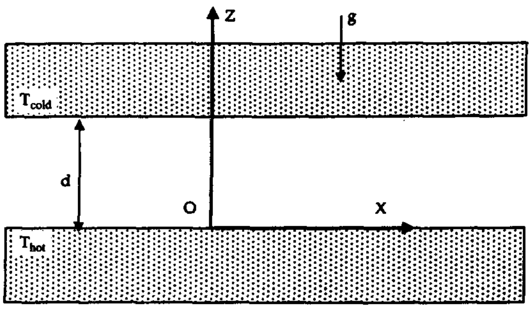

Fig. 1. System of coordinates.

$$\left(\frac{\partial}{\partial t}+v_x\frac{\partial}{\partial x}+v_z\frac{\partial}{\partial z}\right)N_1 = D_{11}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right)N_1 + D^{\mathrm{T}}_{13}N^0_1N^0_3\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right)T$$

$$\left(\frac{\partial}{\partial t}+v_x\frac{\partial}{\partial x}+v_z\frac{\partial}{\partial z}\right)N_2 = D_{22}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right)N_2 + D^{\mathrm{T}}_{23}N^0_2N^0_3\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right)T$$

$$\left(\frac{\partial}{\partial t}+v_x\frac{\partial}{\partial x}+v_z\frac{\partial}{\partial z}\right)\phi = \nu\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right)\phi + \alpha g\frac{\partial T}{\partial x} - g\beta_1\frac{\partial N_1}{\partial x} - g\beta_2\frac{\partial N_2}{\partial x}$$

$$\phi = \frac{\partial v_z}{\partial x} - \frac{\partial v_x}{\partial z}$$

$$\left(\frac{\partial}{\partial t}+v_x\frac{\partial}{\partial x}+v_z\frac{\partial}{\partial z}\right)T = \kappa\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right)T \tag{17}$$

The pressure, as usual, has been eliminated. The product of the mass fractions multiplying the thermal diffusion coefficients is assumed to be constant and to be equal to its initial value, indicated by the superscript 0.

There exists a steady rest state (indicated by the superscript S), together with linear temperature and concentration profiles e.g.

$$N^{\mathrm{S}}_1(z) = N^{\mathrm{S}}_1(0) + z\frac{(N^{\mathrm{S}}_1(d)-N^{\mathrm{S}}_1(0))}{d} \tag{18}$$

and a similar expression for $N^{\mathrm{S}}_2(z)$.

For permeable boundary conditions, N^{S}_1 and N^{S}_2 are imposed at the boundaries $z = 0$ and $z = d$. The vertical component of the mass fluxes is given by

$$J^{\mathrm{S}}_{1z} = -\rho_0\left(D_{11}\frac{N^{\mathrm{S}}_1(d)-N^{\mathrm{S}}_1(0)}{d} + D^{\mathrm{T}}_{13}N^0_1N^0_3\frac{(T_{\mathrm{cold}}-T_{\mathrm{hot}})}{d}\right) \tag{19}$$

and a similar expression for J^{S}_{2z}.

When $N^{\mathrm{S}}_1(0)$ and $N^{\mathrm{S}}_1(d)$ are given (permeable boundary conditions), the mass flux through the liquid layer is also given. On the contrary, for impermeable boundary conditions, $J^{\mathrm{S}}_{1z} = 0$ and therefore, the mass fraction gradient can be calculated

$$\frac{N^{\mathrm{S}}_1(d)-N^{\mathrm{S}}_1(0)}{d} = -\frac{D^{\mathrm{T}}_{13}}{D_{11}}N^0_1N^0_3\frac{(T_{\mathrm{cold}}-T_{\mathrm{hot}})}{d} \tag{20}$$

and is entirely determined by the Soret effect.

To the above steady-state profiles, we add perturbations, we linearize the conservation equations and finally we do a normal mode analysis and write for the different fields

$$F = (N_1, N_2, T, v_x, v_z),$$
$$F(x,z,t) = F^{\mathrm{S}}(z) + \hat{F}(z)\mathrm{e}^{ikx}\mathrm{e}^{\omega t} \tag{21}$$

We get using the notation $\mathrm{d}^n/\mathrm{d}z^n = D^n$:

$$\omega\hat{N}_1 + \frac{N^{\mathrm{S}}_1(d)-N^{\mathrm{S}}_1(0)}{d}\hat{v}_z = D_{11}(D^2-k^2)\hat{N}_1 + D^{\mathrm{T}}_{13}N^0_1N^0_3(D^2-k^2)\hat{T}$$

$$\omega\hat{N}_2 + \frac{N^{\mathrm{S}}_2(d)-N^{\mathrm{S}}_2(0)}{d}\hat{v}_z = D_{22}(D^2-k^2)\hat{N}_2 + D^{\mathrm{T}}_{23}N^0_2N^0_3(D^2-k^2)\hat{T}$$

$$\omega(D^2-k^2)\hat{v}_z = \nu(D^2-k^2)^2\hat{v}_z - \alpha gk^2\hat{T} + \beta_1gk^2\hat{N}_1 + \beta_2gk^2\hat{N}_2$$

$$\omega\hat{T} + \frac{T_{\mathrm{cold}}-T_{\mathrm{hot}}}{d}\hat{v}_z = \kappa(D^2-k^2)\hat{T}. \tag{22}$$

We now use the following scales: d for length, d^2/ν for time, ν/d for velocity, $\Delta T = T_{\mathrm{hot}}-T_{\mathrm{cold}}$ for temperature and $\Delta N_i = N^{\mathrm{S}}_i(d)-N^{\mathrm{S}}_i(0)$ for mass fraction of component i ($i = 1,2$). We shall not use new symbols for the nondimensional quantities. In a nondimensional form, the linearized equations (22) become

$$(D^2-k^2-\omega Sc_1)\hat{N}_1 + Sc_1\hat{v}_z + A_1(D^2-k^2)\hat{T} = 0$$

$$(D^2-k^2-\omega Sc_2)\hat{N}_2 + Sc_2\hat{v}_z + A_2(D^2-k^2)\hat{T} = 0$$

$$Pr(D^2-k^2)(D^2-k^2-\omega)\hat{v}_z + k^2Ra\left(-\hat{T} + \frac{\psi_1}{A_1}\hat{N}_1 + \frac{\psi_2}{A_2}\hat{N}_2\right) = 0$$

$$(D^2-k^2-\omega Pr)\hat{T} + Pr\hat{v}_z = 0 \tag{23}$$

where $Pr = \nu/\kappa$ is the Prandtl number, and for each solute ($i = 1,2$) $Sc_i = \nu/D_{ii}$ are the two Schmidt numbers. ψ_i, the separation ratios, and A_i, are defined below by

$$A_i = \frac{D^{\mathrm{T}}_{i3}}{D_{ii}}N^0_iN^0_3\frac{T_{\mathrm{hot}}-T_{\mathrm{cold}}}{N^{\mathrm{S}}_i(d)-N^{\mathrm{S}}_i(0)}$$

$$\psi_i = \frac{\beta_i}{\alpha}\frac{D^{\mathrm{T}}_{i3}}{D_{ii}}N^0_iN^0_3. \tag{24}$$

When the mass fraction gradients are solely determined by the Soret effect (cf. equation (20)), $A_i = 1$ ($i = 1,2$), otherwise A_i may have any value. In the remainder of the present paper we shall concentrate on the Soret effect, i.e. we shall take $A_i = 1$ ($i = 1,2$).

We have now to adopt boundary conditions. The realistic (i.e. experimental) case of rigid impermeable and conductive boundary conditions is difficult to treat; therefore we take the unrealistic case (but more tractable) of free, permeable and conductive boundary conditions for which

$$\hat{F}(z) = \bar{F}\sin(n\pi z). \tag{25}$$

Substituting the fundamental mode ($n = 1$) for these eigenfunctions into equations (23), we get, for nontrivial solutions to exist (with $x^2 = k^2+\pi^2$).

$$\begin{vmatrix} -(x^2+\omega Sc_1) & 0 & Sc_1 & -x^2 \\ 0 & -(x^2+\omega Sc_2) & Sc_2 & -x^2 \\ k^2Ra\psi_1 & k^2Ra\psi_2 & Prx^2(x^2+\omega) & -k^2Ra \\ 0 & 0 & Pr & -(x^2+\omega Pr) \end{vmatrix} = 0. \tag{26}$$

3.1. *Case of identical diffusion coefficients*

Let us assume $D_{11} = D_{22} = D$, i.e. $Sc_1 = Sc_2 = Sc = \nu/D$. This is a reasonable assumption, since the isothermal diffusion coefficient of isopropanol in water is $\approx 0.87\times10^{-5}$ cm^2 s^{-1} and that of ethanol in water is $\approx 10^{-5}$ cm^2 s^{-1}. In that case equations (26) can be easily transformed into:

$$\begin{vmatrix} -(x^2\omega Sc) & 0 & 0 & 0 \\ 0 & -(x^2+\omega Sc) & Sc & -x^2 \\ k^2Ra\psi_1 & k^2Ra(\psi_1+\psi_2) & Prx^2(x^2+\omega) & -k^2Ra \\ 0 & 0 & Pr & -(x^2+\omega Pr) \end{vmatrix} = 0 \tag{27}$$

implying that the critical Rayleigh number and frequency are determined by the same formulas as those used for a binary mixture (equations (3), (4), (6)), provided that we substitute ψ by the sum $\psi_1+\psi_2$. It can be easily verified that this result also holds for polynary systems of c solutes with

$$\psi = \sum_{i=1}^{c} \psi_i. \tag{28}$$

The critical wave number also remains unchanged $k^{\text{crit}} = \pi/\sqrt{2}$.

3.2. *Case of different diffusion coefficients*

To be complete we now solve the problem with $Sc_1 \neq Sc_2$. Expanding the determinant of equation (26), and looking for a relation between the different nondimensional parameters such that equation (26) is satisfied for $\omega = 0$, we get an expression for the critical Rayleigh number of exchange of stability.

$$Ra^{\text{ex}} = \frac{27\pi^4}{4}\left(1+\psi_1\frac{(Pr+Sc_1)}{Pr}+\psi_2\frac{(Pr+Sc_2)}{Pr}\right)^{-1}. \tag{29}$$

We notice that the equation (29) is equivalent to equation (3) provided that the following change of variables is made in equation (3):

$$\psi = \psi_1+\psi_2$$

$$Sc = Sc_1\frac{\psi_1}{\psi}+Sc_2\frac{\psi_2}{\psi}. \tag{30}$$

In some sense the unique Schmidt number of Section 3.1 has to be replaced by an 'average' Schmidt number. Now we would like to know if equation (4), for the case of overstability, can also be extended to ternary systems with two different Schmidt numbers, with the same change of variables (30). To this end we consider ω purely imaginary. We separate the real and imaginary parts of equation (26), eliminate ω between the two and find an expression for Ra^{over} of the second degree (that we did not try to factorize). Then we take the two Schmidt numbers Sc_1 and Sc_2, two separation ratios ψ_1 and ψ_2 and we seek for the interesting root Ra^{over} of equation (26). Taking $\psi = \psi_1+\psi_2$ and an average Schmidt number as defined above, we compute Ra^{over} thanks to equation (4). We have always found the same values provided that the two Schmidt numbers are not too different. By 'not too different' we mean a ratio not exceeding 5. Some small discrepancies are found when the two Schmidt numbers are totally different, e.g. $Sc_1 = 100$, $Sc_2 = 2000$. Therefore we believe that, when the cross-diffusional effect is neglected, equations (3), (4), (6) and sometimes (7) and (8) give the critical numbers with a sufficient accuracy, provided that we replace ψ and Sc with the rules (30).

4. ESTIMATES APPLIED TO THE WATER–ISOPROPANOL–ETHANOL SYSTEM

We estimate here the critical numbers for a water–isopropanol–ethanol mixture, since the two binary mixtures water–isopropanol and water–ethanol have already been investigated in the laboratory of Mons. Lhost [33] has studied a binary mixture of 90 wt% water–10% isopropanol and found a separation ratio $\psi_1 = -0.44$ (at a mean temperature of 21°C). Touiri [34] investigated a binary mixture of 92 wt% water–8% ethanol for which $\psi_2 = -0.34$ (same mean temperature), in agreement with the value given by Kolodner *et al.* [35]. We cannot crudely add here the two above separation ratios to compute directly the apparent separation ratio of the ternary mixture with equation (28). Indeed, we have to take into account the variation of the different properties like α, β_i and N_i^0 when proceeding from binary to ternary mixtures. However we will assume that the two ratios D_{i3}^{T}/D_{ii} in

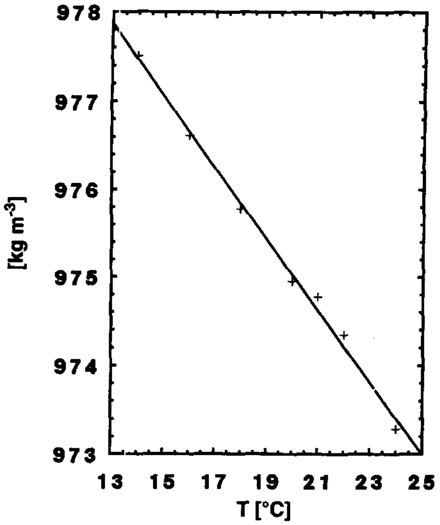

Fig. 2. Temperature variation of the density of the ternary mixture 9.3 wt% isopropanol–7.2 wt% ethanol–83.5 wt% water. The slope is $\alpha = 4.20 \times 10^{-4}$ K^{-1}.

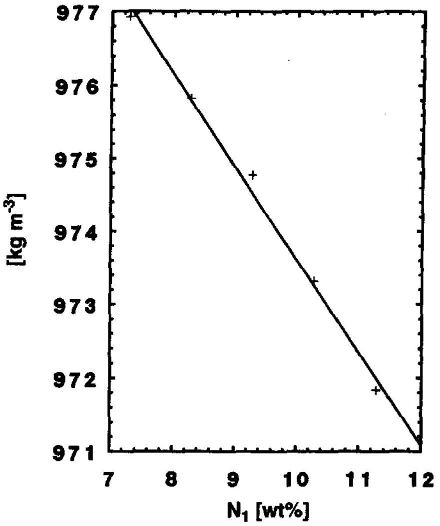

Fig. 3. Density of the ternary mixture water–isopropanol–ethanol at constant temperature 21°C and mass fraction in ethanol (7.2 wt%) vs mass fraction in isopropanol. The slope is $\beta_1 = -0.128$.

the system water–isopropanol–ethanol remain the same as in the two binary mixtures, namely:

$$\psi_1(\text{binary}) = -0.44 \Rightarrow D^{\mathrm{T}}_{13}/D_{11} = 1.20 \times 10^{-2}\mathrm{K}^{-1}$$

$$\psi_2(\text{binary}) = -0.34 \Rightarrow D^{\mathrm{T}}_{23}/D_{22} = 0.78 \times 10^{-2}\mathrm{K}^{-1}. \tag{31}$$

To this end, we have to keep the two water–alcohol mass fraction ratios in the ternary system equal to their values in the two water–alcohol binary mixtures. As a supplementary justification, the quantities D_{ii} and D^{T}_{i3} for our ternary mixture will certainly not be found in tables, and we are not yet prepared to measure these coefficients in our laboratory. Finally, we have already said that the D^{T}_{i3} are less concentration dependent than the Onsager coefficients $a_{i\mathrm{th}}$. This gives us a ternary mixture composed of $N^0_1 = 0.093$ isopropanol–$N^0_2 = 0.072$ ethanol–$N^0_3 = 0.835$ water.

We have measured the density of this ternary mixture vs temperature and composition and get α, β_1 and β_2 (Figs. 2–4). We have also measured the dynamic viscosity η with an Höppler viscosimeter (next $\nu = \eta/\rho$), but λ and C_{P} have been computed from linear laws (like $\lambda = \lambda_1 N_1 + \lambda_2 N_2 + \lambda_3 N_3$) as they are not accessible from tables. Table 1 summarizes all those properties. Next we obtain with equations (24) and (28):

$$\psi_1 = -0.283 \text{ instead of } -0.44$$

$$\psi_2 = -0.153 \text{ instead of } -0.34$$

$$\psi = \psi_1 + \psi_2 = -0.44 \text{ instead of the crude approximation } -0.78. \tag{32}$$

The decrease of each separation ratio ψ_i is due to the decrease of each product $N^0_i\ N^0_3$ compared to the respective binary mixtures, and also from the fact that the ternary mixture composed now of 16.5% of

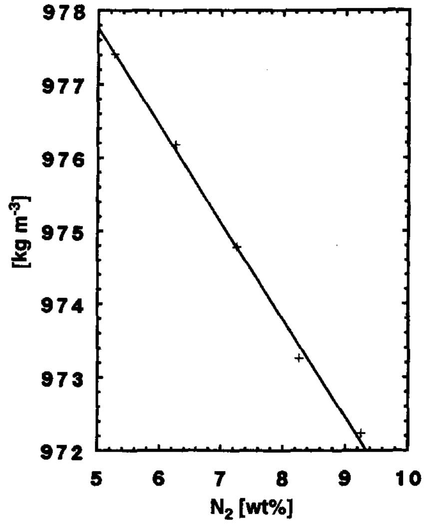

Fig. 4. Density of the ternary mixture water–isopropanol–ethanol at constant temperature 21°C and mass fraction in isopropanol (9.3 wt%) vs mass fraction in ethanol. The slope is $\beta_2 = -0.136$.

Table 1. Summary of the physical properties of the ternary mixture at $T_0 = 21$°C, $N^0_1 = 0.093$, $N^0_2 = 0.072$ and $N^0_3 = 0.835$

ν (m^2 s^{-1})	1.992×10^{-6}
ρ (kg m^{-3})	974.8
α (K^{-1})	4.20×10^{-4}
β_1	-0.128
β_2	-0.136
λ (W m^{-1} K^{-1})	0.52
C_{P} (J kg^{-1} K^{-1})	3.9×10^3
κ (m^2 s^{-1})	1.37×10^{-7}

alcohol is more expansible than the two previous binary mixtures, roughly composed of 10% of alcohol.

Now we are able to compute the critical parameters in the case of rigid, impermeable and conductive boundary conditions, thanks to equations (7) and (8) and to the physical properties of Table 1:

$$r = \frac{Ra^{\mathrm{over}}}{1708} \approx 1.73$$

$$\omega \approx 1.22. \tag{33}$$

For a liquid layer of thickness d = 4.15 mm (see Section 5 below), we can compute the critical temperature difference ΔT_{crit} and the critical period Π_{crit} at the onset of convection:

$$\Delta T_{\mathrm{crit}} = \frac{1708 r\kappa\nu}{g\alpha d^3} = 2.74^\circ\mathrm{C}$$

$$\Pi_{\mathrm{crit}} = \frac{2\pi d^2}{\nu\omega} = 44.5\ \mathrm{s}. \tag{34}$$

We will try to verify these estimates in the following experimental paragraph.

5. LDV EXPERIMENTS AT THE ONSET OF CONVECTION

We run our experiments with a rectangular cell of 4.15 mm thick, 115 mm long and 15 mm large, already described before [36] and used in our earlier experiments in binary mixtures [9–12]. In a preliminary study, using differential interferometry [37], we have observed the travelling waves after the onset of convection in the proposed ternary system. This technique did not allow us to sharply determine the critical period. So we adopt, once again laser Doppler velocimetry (LDV). This is a very precise and non-intrusive technique to provide quantitative velocity profiles and we will not describe LDV here since we use the same apparatus as before. The test experiments on pure water, and on the binary mixture 90% water–10% isopropanol, even if studied intensively before [33] were repeated in the present experimental session and the results are in complete agreement with those of the period 1988–1990. Next we run the experiment on two ternary mixtures of composition very close to the one proposed in paragraph 4 ($N_1^0 = 0.093$ isopropanol–$N_2^0 = 0.072$ ethanol–$N_3^0 = 0.835$ water). The experimental results are summarized in Table 2. For example, taking the mixture $T1$, with the optical probe of the velocimeter set at the centre of the cell, we measured in time the vertical component of the velocity. We get the oscillations given in Fig. 5 when we increase the temperature difference at time $t = 0$ from 1.95 to 1.97°C (trace not given for $t < 4000$). The fast Fourier transform (FFT) of the signal of Fig. 5 (an experimental point is taken each 2 s) performed on 1024 sample points between $t = 4954$ and $t = 7000$ s, gives us a dimensional Hopf frequency of 1.26×10^{-2} Hz. So we deduce the critical period $\Pi_{\mathrm{crit}} = 78.8$ s. Taking the average of the two experimental results (run T_1 and T_2) we get:

$$\Delta T_{\mathrm{crit}} = 2.04^\circ\mathrm{C} \text{ instead of } 2.74^\circ\mathrm{C} \text{ estimated}$$

$$\Pi_{\mathrm{crit}} = 76.0\ \mathrm{s} \text{ instead of } 44.5\ \mathrm{s} \text{ estimated.} \tag{35}$$

There is a complete disagreement between the experimental results and the estimates. Nevertheless, if we compute the separation ratio with equation (7) (knowing the experimental value of $r = 1.26$), and separately with the equation (8) (knowing the experimental value of $\omega = 0.70$), we obtain the same values:

$$\text{from } \Delta T_{\mathrm{crit}} = 2.04^\circ\mathrm{C} \text{ or}$$

$$r = 1.26, \quad \psi = -0.21$$

$$\text{from } \Pi_{\mathrm{crit}} = 76.0\ \mathrm{s} \text{ or}$$

$$\omega = 0.70, \quad \psi = -0.21. \tag{36}$$

Thus the conclusion of our experimental finding is that, in the ternary system, the stabilizing effect seems less than the one estimated, and this will be discussed in Section 7.

6. THE NONLINEAR STATE

When running our experiments in order to determine the critical parameters of the onset of convection, it is rather easy to wait for the nonlinear states of travelling waves (roughly 10 h). For example for the system $T1$, we show a few periods of oscillation of the vertical component of the velocity (Fig. 6), and the FFT of this signal gives a period $\Pi_{\mathrm{TW}} = 487.6$ s. Table 2 summarizes the experimental results on the two ternary systems.

These experimental results are once again surprising. Now the ratio $\omega_{\mathrm{TW}}/\omega_{\mathrm{crit}} = 0.16$, whereas it was of magnitude 0.05 in the binary system. We have no explanation for the moment.

7. DISCUSSION

We have now to seek for an explanation of the discrepancy between the experiments in ternary mixtures and the theoretical predictions given in Section 4.

We believe that the omission of cross-diffusion is the main factor responsible for the observed discrepancy. Indeed from equations (12) and (13) we have at the steady state ($J_1 = J_2 = 0$):

$$\mathrm{grad}(N_1) = \frac{-D_{13}^{\mathrm{T}} N_1 N_3 D_{22} + D_{23}^{\mathrm{T}} N_2 N_3 D_{12}}{D_{11} D_{22} - D_{21} D_{12}} \mathrm{grad}(T) \tag{37}$$

(neglecting once again the term $D_{12}^{\mathrm{T}} N_1 N_2$). A similar expression can be obtained for $\mathrm{grad}(N_2)$. Next writing the steady density gradient, depending on $\mathrm{grad}(T)$

Table 2. Summary of the experiments at a mean temperature of 21°C

Run	wt% water	wt% ethanol	wt% isopropanol
$T1$	83.45	7.26	9.29
$T2$	83.46	7.26	9.28

Run	ΔT_{crit} (K)	Π_{crit} (s)	ω_{crit} (Hz)	Π_{TW} (s)	ω_{TW} (Hz)	$\omega_{TW}/\omega_{crit}$
$T1$	1.96	78.8	1.26×10^{-2}	487.6	2.05×10^{-3}	0.16
$T2$	2.12	73.1	1.37×10^{-2}	465.4	2.15×10^{-3}	0.16

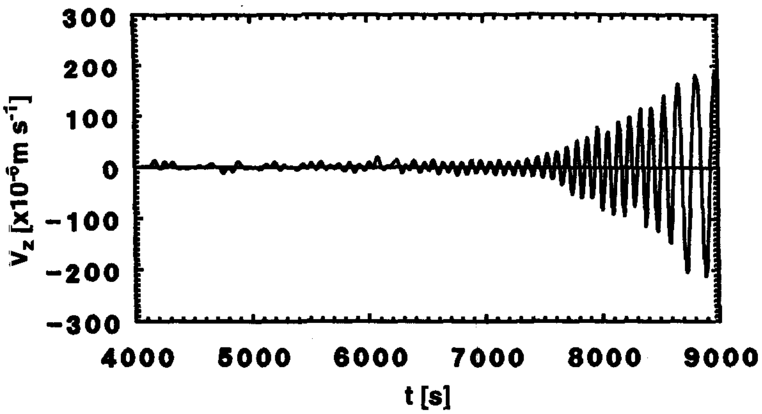

Fig. 5. Onset of convection of the mixture $T1$, when we increase the temperature difference from 1.95 to 1.97°C.

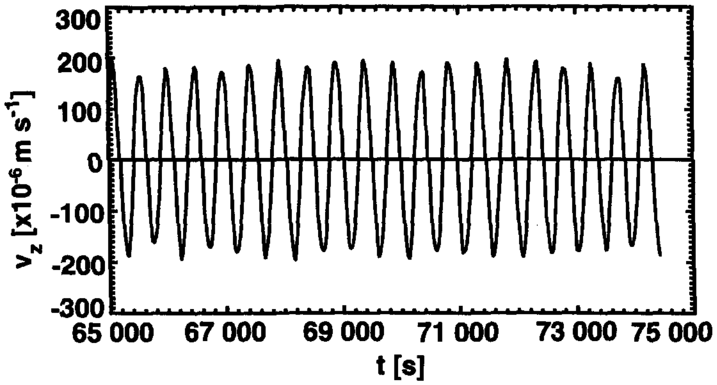

Fig. 6. The state of travelling waves observed on the mixture $T1$, at a temperature difference of 1.97°C.

and on grad(N_i), it can be transformed into equation (38), where ψ_a is an apparent separation ratio of the ternary mixture representing all the contributions of the concentration gradients (including the cross-diffusional effects) to the density gradient.

$$\mathrm{grad}(\rho) = -\rho_0\alpha\,\mathrm{grad}(T)(1+\psi_a) \qquad (38)$$

ψ_a is still equal to $\psi_1+\psi_2$, but now the ψ_i are no longer defined by equation (24). Now they are function of all the coefficients α, β_i, D_{ij}, D^T_{i3} and N^0_i, including cross-diffusional effects.

$$\psi_1 = \frac{\beta_1(D^T_{13}N^0_1N^0_3D_{22}-D^T_{23}N^0_2N^0_3D_{12})}{\alpha(D_{11}D_{22}-D_{12}D_{21})}$$

$$\psi_2 = \frac{\beta_2(D^T_{23}N^0_2N^0_3D_{11}-D^T_{13}N^0_1N^0_3D_{21})}{\alpha(D_{11}D_{22}-D_{12}D_{21})}$$

$$\psi_a = \psi_1+\psi_2. \qquad (39)$$

If the stability of the layer is mainly determined by the steady density gradient, thus by ψ_a, perhaps that the experimental value of $\psi = -0.21$ corresponds to an apparent separation ratio taking into account the

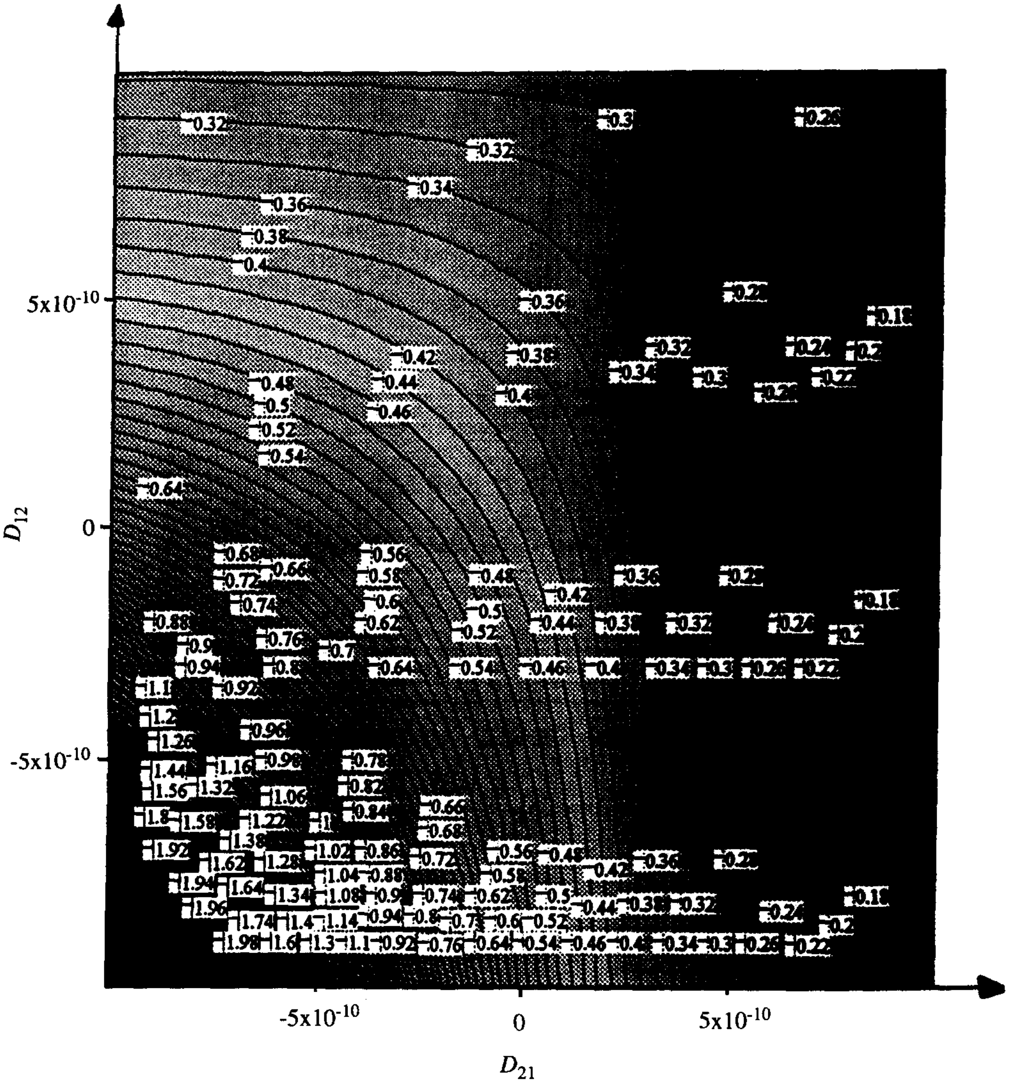

Fig. 7. The apparent separation ratio ψ_a computed in the planes D_{12} and D_{21} (all the other properties are constant and equal to the values given in Table 1).

cross-diffusion. For our ternary mixture, we compute ψ_a as a function of D_{12} and D_{21} (varying between $[-10^{-9}, 10^{-9}]$ $\mathrm{m^2\,s^{-1}}$), and we show that there exist some values of these two cross-diffusional coefficients that could explain a value of $\psi_a = -0.21$ (Fig. 7).

Following this idea, we compute r vs D_{12} and D_{21} with equation (7) ($b = 1$, $Ra^0 = 27\pi^4/4$), in which ψ is equal to ψ_a given by equation (39) (the value of the other properties are fixed). Next we generalize the determinant (26) to include the cross-diffusional effects. The new determinant is written below with A_i defined by equation (24) and $Cr_{ij} = D_{ij}(N_j^S(d) - N_j^S(0))/D_{ii}/(N_i^S(d) - N_i^S(0))$,

$$\begin{vmatrix} -(x^2+\omega Sc_1) & -Cr_{12}x^2 & Sc_1 & -A_1x^2 \\ -Cr_{21}x^2 & -(x^2+\omega Sc_2) & Sc_2 & -A_2x^2 \\ k^2Ra\psi_1 & k^2Ra\psi_2 & Prx^2(x^2+\omega) & -k^2Ra \\ 0 & 0 & Pr & -(x^2+\omega Pr) \end{vmatrix} = 0 \quad (40)$$

from which follows Ra^{over} (or r), that is then compared with the approximation using equations (7) and (39). The agreement is better than 1%.

The conclusion is that for free, permeable and conductive boundary conditions equations (7) and (8), together with an apparent separation ratio given by equation (39), remain a very good approximation, and could also be valid for rigid, impermeable and conductive boundary conditions (at least for comparison with experiments), in ternary systems. If this is true, Fig. 7 shows that the experimental value $\psi_a = -0.21$ can be obtained for different values of

D_{12}, provided that D_{21} is close to 0.8×10^{-9} m^2 s^{-1}, a value not incompatible with reality.

Acknowledgements—This work has been accomplished with the help of Elf Aquitaine (Dr. F. Montel, Pau) and the laboratory MASTER (Prof. Caltagirone, Bordeaux).

REFERENCES

1. D. R. Caldwell, Experimental studies of the onset of thermohaline convection, *J. Fluid Mech.* **64**(2), 347–367 (1974).
2. J. C. Legros, J. K. Platten and P. G. Poty, Stability of a two-component fluid layer heated from below, *Phys. Fluids* **15**(8), 1383 (1972).
3. J. K. Platten and G. Chavepeyer, Oscillatory motion in Bénard cell due to the Soret effect, *J. Fluid Mech.* **60**(2), 305 (1973).
4. R. S. Schechter, M. G. Verlarde and J. K. Platten, The two component Bénard problem, *Adv. Chem. Phys.* **26**, 265 (1974).
5. D. T. J. Hurle and E. Jakeman, Soret-driven thermosolutal convection, *J. Fluid Mech.* **47**(4), 667–687 (1971).
6. V. A. Shteinberg, Convective instability of a binary mixture particularly in the neighbourhood of the critical point, *Prikl. Mat. Mekh.* **35**(2), 375–384 (1971).
7. J. K. Platten and J. C. Legros, *Convection in Liquids*, Chap. 9. Springer, Berlin (1984).
8. D. Villers and J. K. Platten, Heating curves in the two-component Bénard problem, *J. Non-Equilib. Thermodyn.* **9**, 131 (1984).
9. O. Lhost and J. K. Platten, Transitions between steady states, travelling waves, and modulated waves in the system water-isopropanol heated form below, *Phys. Rev. A* **38**(6), 3147 (1988).
10. O. Lhost and J. K. Platten, Experimental study of the transition from nonlinear travelling waves to steady overturning convection in binary mixtures, *Phys. Rev. A* **40**(8), 4552 (1989).
11. O. Lhost and J. K. Platten, Study of large scale convection induced by the Soret effect, *Phys. Rev. A* **40**(11), 4552 (1989).
12. O. Lhost and J. K. Platten, Free convection in binary fluids: sensitivity to lateral boundary conditions, *Phys. Rev. A* **44**(6), 3765 (1991).
13. S. J. Linz and M. Lucke, Convection in binary mixtures: a Galerkin model with impermeable boundary conditions, *Phys. Rev. A* **35**, 3997–4000 (1987).
14. S. J. Linz and M. Lucke, A Galerkin approximation for convection in binary mixtures with realistic concentration boundary conditions, in *Propagation in Non-equilibrium Systems*, Springer Series in Physics, Vol. 41 (Edited by J. E. Wesfried *et al.*), pp. 292–304. Springer, Berlin (1988).
15. S. J. Linz, H. W. Muller, J. Niederlander and M. Lucke, Convection in binary mixtures: travelling waves and lateral currents, *Phys. Rev. A* **38**, 5727–5741 (1988).
16. M. Lucke, Convection in binary mixtures: propagating and standing patterns, in *Non-equilibrium Phase transition*, Lecture Notes in Physics (Edited by Garrido) Springer, Berlin (1988).
17. G. Ahlers and M. Lücke, Some properties of an eight-mode Lorentz model for convection in binary fluids, *Phys. Rev. A* **35**, 470–473 (1987).
18. W. Barten, W. Hort, M. Kamps and M. Lucke, Fully developed travelling wave convection in binary fluid mixtures, *Phys. Rev. Lett.* **63**, 376–379 (1989).
19. C. M. Surko, P. Kolodner, A. Passner and W. Walden, Finite amplitude travelling-wave convection in binary fluid mixtures, *Physica* **23D**, 220–229 (1986).
20. C. M. Surko, P. Kolodner, A. Passner and W. Walden, Rayleigh–Bénard convection in an intermediate-aspect-ratio rectangular container, *J. Fluid Mech.* **163**, 195–226 (1986).
21. C. M. Surko, P. Kolodner and D. Bensimon, Travelling wave convection in an annulus, *Phys. Rev. Lett.* **60**, 1723–1726 (1988).
22. C. M. Surko, P. Kolodner, A. Passner and W. Walden, Onset of oscillatory convection in a binary fluid mixture, *Phys. Rev. Lett.* **56**, 2621–2624 (1986).
23. C. M. Surko, P. Kolodner, A. Passner and H. L. Williams, The transition to finite amplitude travelling waves in binary fluid convection, *Nucl. Phys. B* (proc. Suppl. **2**, 97–108 (1987).
24. E. Moses and V. Steinberg, Competing patterns in a convective binary mixture, *Phys. Rev. Lett.* **57**(16), 2018 (1986).
25. E. Moses and V. Steinberg, *Experiments on Convection in Binary Mixtures, Pattern Defects and Microstructures in Non-equilibrium System, Proceedings of the Nato Advanced Research Workshop*, (Edited by D. Walgraef). Austin, Texas, Academic Press, New York (1987).
26. E. Moses, J. Fineberg and V. Steinberg, Multistability and confined traveling wave patterns in a convecting binary mixture, *Phys. Dev. A* **35**, 2757–2760 (1987).
27. R. W. Griffiths, The influence of a third diffusing component upon the onset of convection, *J. Fluid Mech.* **92**, 659–670 (1979).
28. A. J. Pearlstein, R. M. Harris and G. Terrones, The onset of convective instability in a triply diffusive fluid layer, *J. Fluid Mech.* **202**, 443–465 (1989).
29. G. Terrones and A. J. Pearlstein, The onset of convection in a multicomponent fluid layer, *Phys. Fluids A* **1**(5), 845–853 (1989).
30. A. R. Lopez, L. A. Romero and A. J. Pearlstein, Effect of rigid boundaries on the onset of convective instability in a triply diffusive fluid layer, *Phys. Fluids A* **2**(6), 897–902 (1990).
31. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids.* Wiley, New York (1954/1964).
32. T. G. McDougall, Double diffusive convection caused by coupled molecular diffusion, *J. Fluid Mech.* **126**, 379–397 (1983).
33. O. Lhost, Etude de la convection libre induite par effet Soret, Ph.D. Thesis, Faculty of Sciences, University of Mons-Hainaut, Belgium (1990).
34. H. Touiri, Contribution à la convection avec effet Soret: effect du rapport de séparation, Ph.D. thesis, Faculty of Sciences, University of Mons-Hainaut, Belgium (1992).
35. P. Kolodner, H. Williams and C. Moe, Optical measurement of the Soret coefficient of ethanol–water solutions, *J. Chem. Phys.* **88**, 6512–6524 (1988).
36. J. K. Platten, D. Villers and O. Lhost, *Laser Doppler Anemometry in Fluid Mechanics* (Edited by R. J. Adrian, T. Asanuma, D. F. G. Durao, F. Durst and J. H. Whitelaw), Vol. 3, pp. 245–260. Instituto Superior Technico, Lisbon (1988).
37. J. P. Larre, J. K. Platten and G. Chavepeyer, Convection thermique en milieu fluide dans un mélange polynaire, *Entropie* **184/185**, 53–56 (1994).