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Experimental investigation of gravity-induced concentration gradients in critical mixtures

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Abstract. The building up of concentration gradients in a critical mixture of aniline and cyclohexane is observed. We use a non-perturbative technique that allows the observation of the gradients along the entire size of the sample. The experiments are performed at three temperatures, i.e. $(T - T_c)/T_c = 1.8 \times 10^{-3}$, 6.0×10^{-4} and 2.3×10^{-4} . The experimental results allow the calculation of the magnitude of the barodiffusion coefficients and of the osmotic compressibility, as well as their critical behaviour. In addition, for the first time to our knowledge, the Onsager coefficient can also be evaluated.

The experimental results are discussed in the framework of existing theories, especially as far as the state equation of the system is concerned. It is shown that the observed values are close to theoretical predictions both in magnitude and temperature dependence. However, a detailed analysis of the results shows some unexpected peculiarities that cannot be explained in terms of the existing theories. We briefly discuss these peculiarities and suggest some possible explanations.

1. Introduction

It is well known that very large density gradients arise in a fluid near its gas-liquid critical point. However, in critical mixtures the building up of concentration gradient takes place in the neighbourhood of the consolute critical point. It has to be noted that as far as the gas-liquid critical point is concerned, the order parameter (i.e. the mass density of the fluid) directly couples with the gravitational field. The strong divergence of the isothermal compressibility is therefore directly implied in the building up of the density gradient.

In a critical mixture, however, the order parameter is the concentration and the strong divergent quantity is the osmotic compressibility. The coupling with the gravitational field only takes place because of the difference in the mass density of the two components. In addition, in a mixture other concomitant phenomena can take place, namely the Soret and the Dufour effect, as we shall discuss in the next section.

From the experimental point of view, the phenomenon was investigated by Greer *et al* (1975). The density gradient was measured with a magnetic densitometer (spherical buoy, 1 cm diameter). The measuring procedure, however, implies an unwanted stirring of the sample. In addition a 1 cm thick layer cannot be investigated both in the upper and lower part of the cell. In such a work only one temperature is investigated.

An optical method has been used more recently (Giglio and Vendramini 1975, to be referred to as II). In this work the concentration gradient is calculated from the bending of a light beam passing through the sample. It seems, however, that only a central layer

of the sample is investigated by the authors. It has to be noted that, unless the mean concentration of the sample exactly corresponds to the critical one, the concentration in the explored layer will change in the course of time.

In the present paper we report measurements performed with a non-perturbative optical technique that allows for the evaluation of the gradients over the entire size of the cell. Measurements are performed at three different temperatures, so that the critical behaviour of the implied quantities can be deduced. A preliminary report, concerning only one temperature, has been published elsewhere (Maisano *et al* 1976).

2. Preliminary considerations

As far as the barodiffusion is concerned, two kinds of calculation can be performed. In the first one, the system is described in its equilibrium state, taking into account the gravitational contribution to the chemical potential of the components (Mistura 1971). In such a case no information is available concerning the evolution of the gradients, the magnitude of the time constants and the influence of crossed transport phenomena.

A different approach consists in starting from the flux equations and then searching for the asymptotic stationary solutions. The flux equation can be written as follows (Landau and Lifshitz 1959):

$$\mathbf{J} = -\rho D \left(\text{grad } c + \frac{k_T}{T} \text{grad } T + \frac{k_P}{P} \text{grad } P \right). \quad (1)$$

In equation (1), c is the mass concentration, k_T the thermal diffusion ratio, that accounts for the Soret effect, k_P the barodiffusion ratio, and D the diffusion coefficient, the other symbols having their usual meanings.

First of all we try to compare the contributions to the total flux given by the thermal diffusion and the barodiffusion. For the mixture aniline-cyclohexane, with which we are concerned in the present work, the thermal diffusion ratio has been recently evaluated (Giglio and Vendramini 1975, to be referred to as I). The barodiffusion ratio is given by:

$$k_P = P \frac{(\partial V / \partial c)_{P,T}}{(\partial \mu / \partial c)_{P,T}} \quad (2)$$

where V is the specific volume and μ the Landau chemical potential. The value of $(\partial \mu / \partial c)$ can be taken from the literature (Calmettes *et al* 1972, II). At $(T - T_c) = 0.5$ K one gets $(\partial \mu / \partial c) = 6.2 \times 10^5$ erg g⁻¹. In addition

$$\left(\frac{\partial V}{\partial c} \right)_{P,T} = \frac{1}{\rho_1} - \frac{1}{\rho_2} \cong 0.3 \text{ cm}^3 \text{ g}^{-1},$$

ρ_1 and ρ_2 being the densities of the two components, so that one obtains $(k_P/P) \text{ grad } P \cong 4.15 \times 10^{-4} \text{ cm}^{-1}$. At the same temperature, k_T (from I) turns out to be 30. It follows that the quantity $(k_T/T) \text{ grad } T$ assumes the same values of $4.15 \times 10^{-4} \text{ cm}^{-1}$, for a temperature gradient $\text{grad } T = 4.15 \times 10^{-3} \text{ K cm}^{-1}$.

As a consequence, in order to avoid a spurious Soret effect it is enough to ensure a thermoregulation better than 10^{-3} K, so that gradients of comparable magnitude cannot arise. As the critical point is approached, both k_P and k_T diverge. As we shall see, k_P diverges like $\epsilon^{-1.3}$, ϵ being the reduced temperature $(T - T_c)/T_c$.

As far as k_T is concerned, a similar power law was suggested (Thomaes 1956) while more recently Giglio (I) argued a less strong divergence, i.e. $k_T \cong \epsilon^{-0.73}$. In every case as the critical point is approached, the above mentioned condition for the thermostata-tion maintains its validity or becomes even less severe. However, as we shall see below, the fact that some local Soret effect could take place cannot be excluded, in spite of such a limitation, near the boundaries of the cell.

As far as the heat flux connected with the flux of matter is concerned (Dufour effect), it can be shown that, taking into account the appropriate boundary conditions, a temperature gradient arises which is smaller than 10^{-6} K, so that the effect can be completely neglected.

Therefore, in our experimental conditions, the flux equation can simply be written as:

$$\mathbf{J} = -\rho D \left(\text{grad } c + \frac{k_P}{P} \text{grad } P \right). \quad (3)$$

Equation (3) can also be written in terms of the molar concentration of one component, x_1 , and of its chemical potential μ_1 . One has to take into account that

$$D = \frac{\alpha}{\rho} \left(\frac{\partial \mu}{\partial c} \right)_{P,T} \quad (4)$$

where α is the appropriate Onsager kinetic coefficient, and that

$$\mu^c = (\mu_1/M_1) - (\mu_2/M_2) \quad (5)$$

where M_1 and M_2 are the molar masses of the two components. Making use of the Gibbs-Duhem relation $x_1 d\mu_1 + (1-x_1) d\mu_2 = 0$ one gets:

$$\left(\frac{\partial \mu}{\partial c} \right)_{P,T} \text{grad } c = \left(\frac{\partial \mu}{\partial x_1} \right) \text{grad } x_1 = \left(\frac{1}{M_1} + \frac{x_1}{1-x_1} \frac{1}{M_2} \right) \frac{\partial \mu_1}{\partial x_1} \text{grad } x_1 \quad (6)$$

and equation (3) can be written, after some algebra:

$$\mathbf{J} = -\alpha \left(\frac{1}{M_1} + \frac{x_1}{1-x_1} \frac{1}{M_2} \right) \left[\left(\frac{\partial \mu_1}{\partial x_1} \right)_{P,T} \text{grad } x_1 + \left(V_1 - \frac{M_1}{\rho} \right) \text{grad } P \right] \quad (7)$$

where V_1 is the molar volume of the first component.

When a stationary state is reached, i.e. when the flux of matter vanishes, a concentration gradient exists in the mixture, given by

$$\text{grad } x_1 = - \left(V_1 - \frac{M_1}{\rho} \right) \text{grad } P \left(\frac{\partial \mu_1}{\partial x_1} \right)_{P,T}^{-1} \quad (8)$$

or, equivalently, from equation (3):

$$\text{grad } c = \left(\frac{\partial V}{\partial c} \right)_{P,T} \text{grad } P \left(\frac{\partial \mu}{\partial c} \right)_{P,T}^{-1}. \quad (9)$$

3. Experimental set-up and procedure

We measure the concentration gradients in a critical mixture of aniline and cyclohexane by means of an optical method. Great care is taken to fill the cell as exactly as possible at the critical concentration. The criterion that we use is similar to that suggested by

Balzarini (1974) and consists essentially in the requirement that, if the temperature is slowly lowered, starting from the one-phase region, the meniscus appears in the cell at exactly one-half of the height.

We use an optical cell shaped as a parallelepiped of $(1 \times 2 \times 4) \text{ cm}^3$. The plane parallel surfaces of $(1 \times 4) \text{ cm}^2$ are bound to two cylinders of fused silica in order to ensure the optical accessibility of the sample, together with a good thermoregulation (Cannistraci *et al* 1972). In figure 1 the experimental set-up is schematically shown. B is a large thermostatic bath, driven by a proportional control system that ensures a stability better than $0.5 \times 10^{-3} \text{ K}$, both in the magnitude and gradients of temperature across the cell C. T is a platinum thermometer that acts as a sensor for the control system, through a bridge whose unbalance signal, suitably amplified, drives the heater H. The cooling source is supplied by a separate thermostatic bath. The temperature in the cell is monitored through a calibrated NTC sensor together with a Müller bridge. The broken line in the bath indicates the streamlines of the thermostatic fluid propelled by the stirrers E.

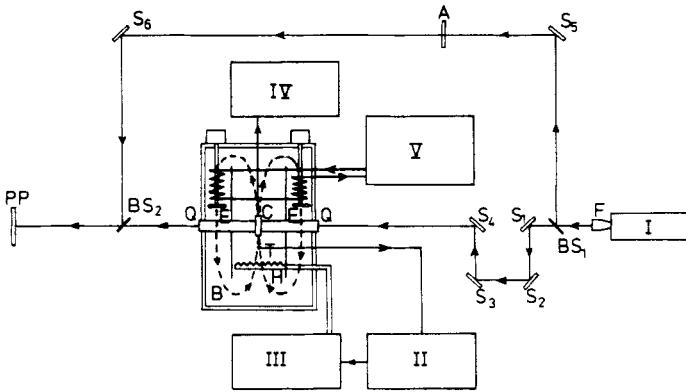


Figure 1. Schematic drawing of the experimental set-up. I, He-Ne SmW laser; II, L-N ER bridge and null detector; III, current amplifier; IV, L-N Müller bridge; V, Haake thermostatic bath ($\pm 0.02^\circ \text{C}$).

Q denotes the two cylinders of fused silica that allow a good thermostatisation of the sample, together with the required optical accessibility. The optical arrangement (mirrors S and beam splitters BS) constitutes a Mach-Zender interferometer. F is a telescope that furnishes a plane wave of cross section larger than the cell size. The mirrors S_1 - S_4 are used in order to equalize the optical path of the two beams, taking into account the refractive index of fused silica. This arrangement, together with the variable attenuator A, ensures maximum fringe contrast. The mirror S_6 can be tilted in order to adjust the angle between the two beams, so that a pattern of fringes of given spacing is produced on the screen PP. As long as the sample in the cell is homogeneous, the fringes are selected to be straight and vertical. If, however, the sample ceases to be homogeneous, the fringe pattern changes, so that the variation of refractive index in the sample can be evaluated from the displacement of the fringes. It can easily be shown that:

$$\delta n = \frac{\pi}{k_0 d} \frac{\delta s}{\Delta} = \frac{\lambda_0}{2d} \frac{\delta s}{\Delta} \quad (10)$$

where δn is the variation of the refractive index, Δ is the interfringe spacing, k_0 and λ_0 are respectively the wavevector and the wavelength of the radiation in the vacuum, δs is the horizontal displacement of the fringes, and d is the depth of liquid travelled by the wave ($d = 2$ cm).

It can be shown (Balzarini 1974) that the variations of the refractive index can be taken as proportional to the variation of concentration. In the case of the aniline-cyclohexane one can write $\delta n = 0.114\delta x_1$ with an approximation better than 1%.

We have also taken into account the estimation of refractive errors in the deflection of the beam (Anderson *et al* 1975). In our case, however, this kind of correction is completely negligible.

The measurements are performed as follows. First of all the temperature of the bath is stabilized at a given value. Then the sample is carefully stirred until a homogeneous state is reached. As a consequence the fringe pattern appears to be rigorously vertical. As the time increases, a concentration gradient builds up, so that the fringes show departure from the vertical. The fringe pattern is photographically recorded, at time intervals of about one day, until no detectable difference appears between two successive records: in this case we assume that the system is very close to its stationary state.

We perform measurements at three temperatures, i.e. at $(T - T_c) = 0.54, 0.19$ and 0.07 K respectively. The experimental data concerning the value $(T - T_c) = 0.19$ K has been reported elsewhere (Maisano *et al* 1976), where some typical photographic reproductions of the fringe pattern are also shown.

4. Discussion of experimental results

The experimental results are reported in figure 2. Here we report in the abscissae the variation of the molar concentration, and in the ordinate the height in the cell. The various curves refer to increasing time after the stirring. For the sake of clarity, only a small number of curves are reproduced. The last one refers to the stationary situation, after which no further changes are found. The origin in the abscissae scale is fixed in such a way that the mean concentration variation over the entire height of the cell will be zero.

The results can be discussed both from the point of view of the temperature dependence of the phenomenon and from the point of view of the geometrical behaviour of the gradients. As far as the temperature dependence is concerned, one can evaluate a mean value of the gradients in the stationary state, so that the order of magnitude of the barodiffusion coefficient k_p can be plotted as a function of temperature.

This is done in figure 3 (full circles and line). The points fall onto a straight line whose slope can be evaluated giving a value of -1.3 . This result agrees with the theoretical prediction, for k_p being inversely proportional to the thermodynamic derivative $(\partial\mu/\partial x_1)_{P,T}$ that is known to behave like ϵ^γ . The magnitude of $(\partial\mu/\partial x_1)_{P,T}$ can also be calculated (see figure 3, open circles and broken line) and gives values that practically coincide with previous measurements (Calmettes *et al* 1972, II). The latter circumstance strongly supports the assumption that in our measurements the system reaches a state that is very close to the stationary one.

We also tried to evaluate the behaviour of the Onsager coefficient α that appears in equation (4) from our experimental data. We measured the concentration gradients at

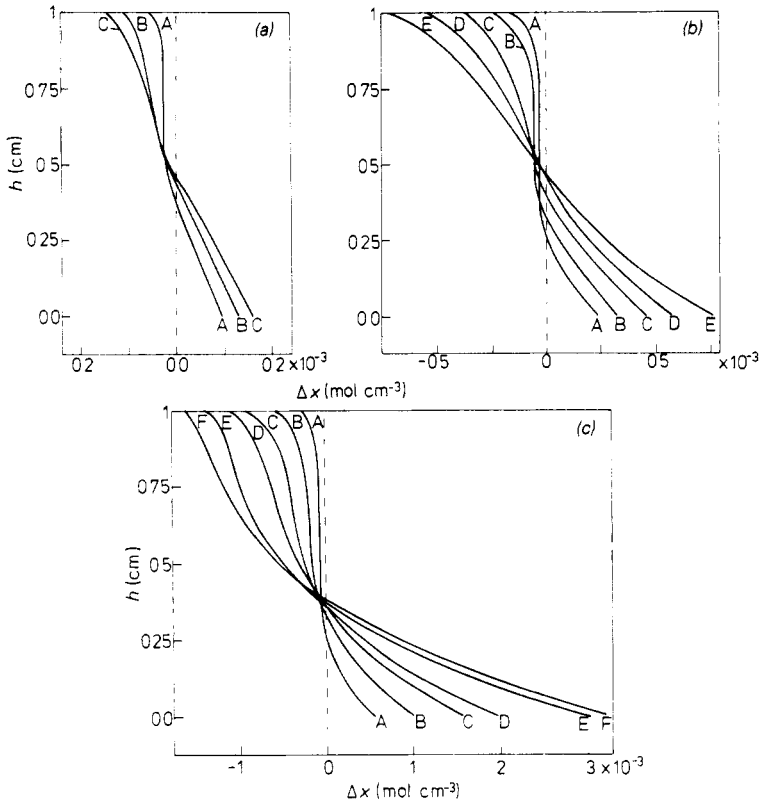


Figure 2. Variation of concentration as a function of height, at various times after stirring for (a) $(T - T_c)/T_c = 1.8 \times 10^{-3}$; A = 52 h; B = 101 h; C = 144 h; (b) $(T - T_c)/T_c = 6 \times 10^{-4}$; A = 48 h; B = 96 h; C = 192 h; D = 288 h; E = 396 h; (c) $(T - T_c)/T_c = 2.3 \times 10^{-4}$; A = 75 h; B = 171 h; C = 267 h; D = 364 h; E = 457 h; F = 505 h.

the very beginning of the barodiffusion process, i.e. when the magnitude of the gradient itself was very small. In this case, the first terms on the right-hand side of equation (3) can be neglected, and the flux can be attributed only to the barodiffusion process, i.e.:

$$\mathbf{J} \cong -\alpha(\partial V/\partial c)_{P,T} \text{grad } P. \quad (11)$$

The flux \mathbf{J} can be roughly evaluated from the variation of the concentration (at short times) in the lower part of the cell, so that α can be calculated.

The values obtained are plotted in figure 4 (full squares and broken line). It can be seen that the three data points fall onto a straight line, whose slope is -0.66 . Again, such a result agrees with the theoretical predictions, because the Onsager coefficient is known to diverge with the critical exponent (Sengers 1972, Papoular 1974). To our knowledge this is the first direct observation of the critical behaviour of the Onsager coefficient. As far as the magnitude of α is concerned, it can be calculated from equation (4), using for the diffusion coefficient D the data available from literature (Berge *et al* 1969), and for the thermodynamic derivative $(\partial\mu/\partial c)_{P,T}$ the present data as well as those (practically coincident) of the literature (Calmettes *et al* 1972, II). It can be seen that one obtains values that are roughly one-half of those evaluated with the above mentioned procedure (open squares in figure 4). Due to the rather crude

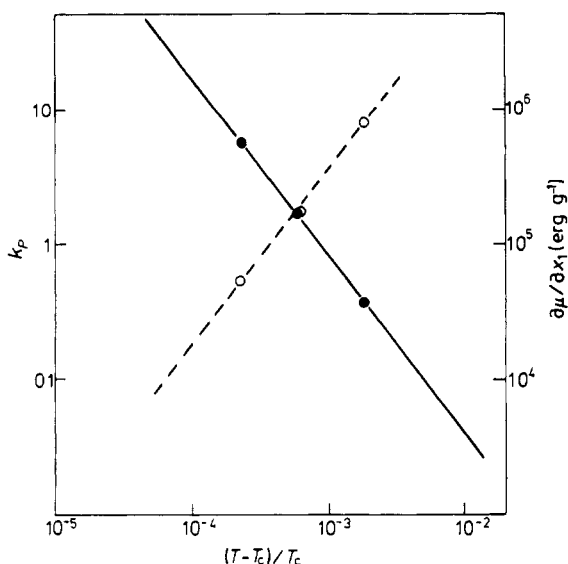


Figure 3. Barodiffusion coefficient k_P (full line, scale on the left, slope -1.3) and osmotic compressibility $(\partial\mu/\partial x_1)_{T,P}$ (broken line, scale on the right, slope $+1.3$) as a function of the reduced temperature.

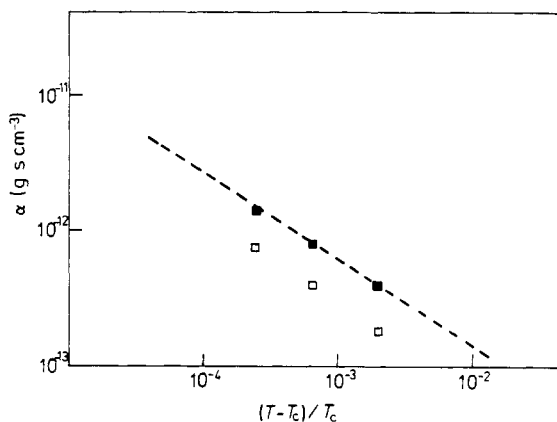


Figure 4. Onsager coefficient as a function of reduced temperature. Full square, experimental point; open square, values calculated from equation (4); slope of broken line, -0.66 .

method used for the evaluation of the flux, we consider this order-of-magnitude agreement as satisfactory. We cannot exclude, however, the fact that the sedimentation of the denser component can actually be faster than that predicted from equation (3). This point of view could be confirmed by the circumstance that the time required for the system to reach a stationary state turns out to be smaller than that theoretically predicted.

In fact the characteristic time constant of the phenomenon can be evaluated (II) from the equation:

$$\tau = h^2 / \pi^2 D \tag{12}$$

where $h = 1$ cm is the height of the cell. At the three temperatures investigated one gets for τ the values of 7.8, 15.3 and 27.6 days respectively. One would expect that the system practically reaches the stationary state after a time of the order of $2-3\tau$. On the contrary, from the experimental results no further variations are found in the system after a time of 6, 16 and 21 days respectively, that are times even less than the calculated values of τ . A similar circumstance is pointed out by Giglio and Vendramini (II), concerning the data of Greer *et al* (1975). Let us now briefly discuss the geometrical shape of the gradients. Some peculiarities are to be stressed:

(i) The building up of the gradients begins with a precipitation of the denser component that takes place in a nearly uniform way over the entire upper part of the cell.

(ii) The stationary shape of the gradients shows noticeable departures from a straight line.

(iii) The gradient appears asymmetrical with respect to the centre of the cell.

(iv) The magnitude of the gradients increases near the upper and lower boundary of the cell.

The latter three circumstances can also be shown in the data of Greer *et al* (1975).

From equations (8) and (9) it can be shown that the shapes of the gradients depend on the state equation:

$$(\partial\mu/\partial c)_{P,T} = f(c, T) \quad (13)$$

so that the departure from linearity indicates a dependence of the thermodynamic derivative upon the concentration. One can try to write a classical equation of state of the kind suggested by Voronel' and Giterman (1965):

$$(\partial\mu/\partial c)_{P,T} = A(T) + \frac{1}{2}B(c - c^*)^2 \quad (14)$$

where c^* is the critical concentration, and:

$$A(T) = (\partial\mu/\partial c)_{c=c^*}, \quad B = (\partial^3\mu/\partial c^3)_{c=c^*}. \quad (15)$$

Inserting equation (14) in equation (9) and integrating one gets for the stationary shape of the gradient, the following expression:

$$A(c - c^*) + \frac{1}{6}B(c - c^*)^3 = \left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)\rho g(h - h^*) \quad (16)$$

where h^* is the height at which $c = c^*$.

From equation (16) it appears that the maximum value of the gradient corresponds to the height h^* . However, the latter would be the centre of the cell only if the mean concentration corresponded exactly to the critical one. Even a very small deviation can destroy such a symmetrical behaviour. As an example one can consider the curve F of figure 2(c). The maximum value of the gradient is obtained near the bottom of the cell, so that curve F turns out to be consistent with equation (16) if one assumes that the mean concentration differs from the critical one by an amount of only 2×10^{-3} . If this is the case, one gets for A a value of about 2.3×10^4 erg g⁻¹. In figure 5 we plot equation (16) for different values of the parameter B . The broken rectangle reproduces the height of the cell and the total variation of the concentration experimentally found (curve F of figure 2(c)). It can be shown that the theoretical curve corresponding to a value of B of 2×10^{10} erg g⁻¹ exactly reproduces the experimental behaviour, also as far as the height at which the concentration assumes its mean value is concerned (full line inside the rectangle). To our knowledge no data concerning the values of B exist in the

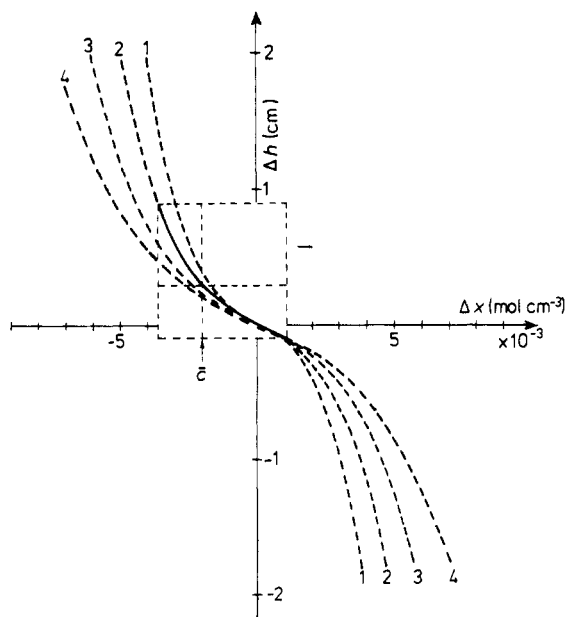


Figure 5. Theoretical shape of concentration gradient, calculated from equation (16). In the broken rectangle, the full line represent the experimental results. $A = 2.3 \times 10^4 \text{ erg g}^{-1}$; $c - \bar{c} = 2 \times 10^{-3}$; 1, $B = 4 \times 10^{10} \text{ erg g}^{-1}$; 2, $B = 2 \times 10^{10} \text{ erg g}^{-1}$; 3, $B = 1 \times 10^{10} \text{ erg g}^{-1}$; 4, $B = 0.5 \times 10^{10} \text{ erg g}^{-1}$.

literature for the system aniline–cyclohexane, however the value of $2 \times 10^{10} \text{ erg g}^{-1}$ seems to be of the correct order of magnitude (Voronel' and Giterman 1965).

In our opinion, therefore, one cannot exclude that the asymmetrical behaviour is due to even a small variation of the mean concentration with respect to the critical one.

An alternative explanation of the observed peculiarities can be as follows: although in our experimental apparatus fluctuation of temperatures larger than 0.5×10^{-3} are avoided, one cannot exclude the possibility that temperature gradients of the order of some millidegrees per centimetre can arise near the boundaries of the cell. Actually the thermoregulation of the sample is obtained through a continuous flow of fluid (vaseline oil) whose temperature is monitored by the probe T (see figure 1). The unbalance signal, suitably amplified, drives the heater H. In the interior of the sample, however, only a thermal diffusion process can take place in order to ensure thermal equilibrium. As such a process takes rather a long time, any change in the temperature of the flowing thermostatic bath would result in an unavoidable temperature gradient across the boundaries of the sample. Such an effect could be more relevant as far as the lower part of the cell is concerned, because this is the first one struck by the thermostatic flux.

As a consequence the Soret effect would act as a pump that drags the denser component towards the walls of the cell. In turn this circumstance would result in a lowering of the time needed to reach the stationary state and could explain both the depletion of the sender component along the height of the cell and the anomalous increase of the concentration gradients across the walls.

At the present we are not able either to decide about one of the two proposed mechanisms, or to exclude that the observed anomalies could have a deeper meaning, in connection with the physical description of the critical system.

5. Conclusion

We measured the phenomenon of barodiffusion in a critical mixture. The measurements, performed with an optical interference method, allow for the detection of the concentration gradients with a non-perturbative technique along the entire size of the cell.

From the experimental results, the appearance of gradients is quite evident. Their size, as well as their temperature dependence, allows for the calculation of the barodiffusion coefficient, and of the osmotic compressibility. The results obtained agree well with previous data and confirm the critical behaviour of these quantities. In addition, one can also evaluate the Onsager coefficient associated with a phenomenon. As a result one obtains the result that this coefficient diverges with a critical exponent 0.66, in good agreement with current theories.

As far as the detailed behaviour of the gradients is concerned, some anomalies are observed. We show that these anomalies could be started either by even a very small deviation of the mean concentration compared with the critical one, or by the building up of local temperature gradients near the walls of the cell. However, we cannot exclude that some physical peculiarities of the critical system, up to now not considered, could be at the origin of the observed peculiarities. More refined measurements are needed and are in progress at present in order to clarify this point.

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