Convective Instabilities and Dynamic Structures in Phase-Separation Processes of Binary Liquid Mixtures

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In pressure jump experiments on the phase separation of binary liquid mixtures of cyclohexane + methanol, an organisation of the finely dispersed precipitate could be observed to give a macroscopic dissipative structure during the early stages of the ageing process of the newly formed phase. Preliminary phenomenological investigations suggest a mechanism similar to the Rayleigh-Bénard instability (RBI) and the Soret-driven instability (SDI).

If a horizontal layer of a fluid with a vertical depth d is submitted to a temperature gradient ΔT directed downward, convective motion sets in if ΔT exceeds a critical value ΔT_{crit}. For pure fluids, the threshold of the onset of this motion and other properties are strongly related to the Rayleigh number [1, 2].

$$\text{Ra} = \frac{\alpha g \Delta T}{\nu \varkappa} d^3,$$

where α = cubic expansion coefficients, ν = cinematic viscosity, $\varkappa$ = thermal diffusivity, g = acceleration due to gravity (see below).

In fluid mixtures often another kind of convective instability is observed, depending on a concentration gradient in addition to the temperature gradient. Due to the fact that spatial inhomogenities in concentration have a longer lifetime than temperature inhomogenities, the buoyancy forces mainly depend on the concentration profile [3].

More complicated relations have to be expected in a liquid layer, modelled by a system of two freshly separated liquid phases. All the more it might appear remarkable that the visible structure of a nascent convective instability in this system essentially shows the pattern of the Rayleigh-Bénard instability with hexagonal structures.

In this work, the phenomenon was observed in the system cyclohexane + methanol. This mixture is completely miscible above its upper critical solution temperature T_c^u of about 47 °C at normal pressure.

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T_c^u increases with increasing pressure (by about 0.1 K · MPa^{-1}). The difference of densities between coexisting separated phases is less than 0.01 g · cm^{-3}; i.e. the system behaves nearly isopycnic. By a fast pressure pulse (5 MPa in 10 ms; temperature 39 °C) in a pressure-jump vessel with cylindrical geometry mounted below a microscope (for details see [4]) the transition from homogeneous to heterogeneous liquid state was achieved. After the pressure jump the cell windows were obscured by fine aggregates of the new phase. Within a few minutes the system again became transparent to some extent: Between dark, unregularly shaped regions, transparent channels were visible, containing negligible few droplets of precipitate. These structures became well defined with sharp boundaries and then vanished within a period of typically 10 min to show a diffuse pattern.

To confirm the supposition that this dissipative structure is due to a hydrodynamic instability closely related to the Rayleigh-Bénard instability, some additional experiments with variation of the layer-depth of the liquid system under test were carried out. Typical dimensions of this convection are demonstrated by Fig. 1 a and 1 b where the layer-depth is 2 mm or 0.8 mm respectively. The dimensions of the structures are in the order of magnitude of the actual distances between cell windows; they amount to 2–3 mm in Fig. 1 a and 0.5–1 mm in Figure 1 b. Investigations of other authors [5] concerning the velocity profile of the Rayleigh-Bénard instability showed that the locus of maximum velocity of material transport in a hexagon-structure slightly beyond its threshold is $2d$ apart from the corresponding locus of another hexagon-structure.

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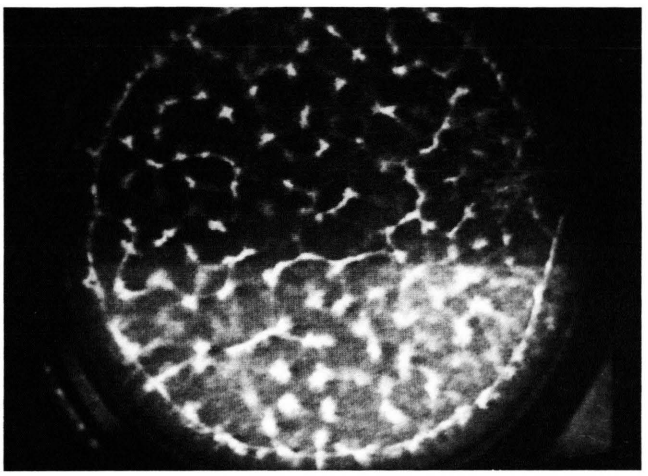

Fig. 1 a. Upper window of microscope cell seen from above. The specimen consists of a 2 mm film of demixed cyclohexane + methanol system. Since pressure-jump induced phase separation a period of 5 min has passed. Structuration divides the system into dark clouds of droplets and bright channels containing very few droplets (diameter of cell window: 22 mm).

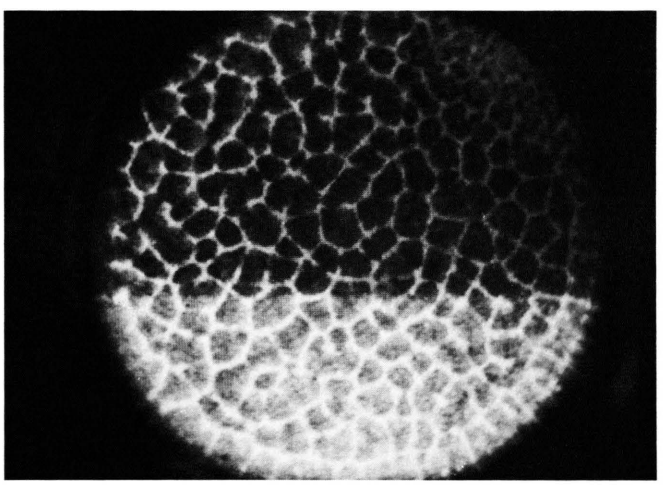

Fig. 1 b. Same as Fig. 1 a, but 0.8 mm film.

The geometry of the pattern in Figs. 1 a and 1 b matches this order of magnitude; hence we may deduce that the structures are primarily caused by an instability closely related to Rayleigh-Bénard instability. A further reduction of cell-window distance consistently resulted in a reduced size of the structures. However, the stronger influence of lateral wall-effects and experimental difficulties caused disturbances in structure development and bad optical resolution in experiments with cell depths of 0.4 mm. A microscopic enlargement of details of Fig. 1 b revealed that the dark areas consisted of small droplets gyrating vertically of course detectable by a quick-motion apparatus only.

The temperature gradient amounts to about 0.5 K between upper and lower cell window in both experiments. This is only a rough estimate because up to now it was not possible to carry out exact measurements of the temperature difference within the cell volume. It has to be expected, however, that the magnitude of the temperature gradient within the cell volume is smaller though the thermal contact with temperature fields above and below the cell is favoured by the sapphire windows.

Further investigations aimed on an adjustment of isopycnic behaviour of the system. But it is hardly possible to find a binary liquid system that matches isopycnic conditions when undergoing phase separation. Therefore a small amount of a third component was added to the binary mixture in order to get equal densities of the separated phases. It was found [6] that the density difference of coexisting

liquid phases of the system cyclohexane + methanol is reduced to about 0.001 $g \cdot cm^{-3}$ by addition of about 1 mol% tetrachloroethene; the amount of C_2Cl_4 necessary to obtain complete equality of densities varies for every combination of p, T and x of the system because of changes in compressibilities and cubic expansion coefficients. It may be of some interest to note that no structures were obtained in a system containing C_2Cl_4 in order to improve the isopycnic behaviour. In systems with larger density differences than those used in Fig. 1 (e.g. in 2-butoxyethanol + water) also no tendency could be observed to the development of structures described above. A small but not negligible density difference of the separated phases seems to be necessary to initiate this kind of convective motion. Similar phenomena might be expected under the influence of reduced gravity with correspondingly larger density differences (i.e. 10 $g \cdot cm^{-3}$ at a residual acceleration of 0.001 g instead of 0.01 $g \cdot cm^{-3}$ at normal acceleration).

From the fact that a homogeneous dispersion is precipitated in the initial stages of phase separation it is evident that neither during this stage nor before the induction of the phase separation (here by a pressure jump) any convective motion has developed in the cell volume. So the structuration process is casually attributed to the ageing process of the precipitate. The influence of adiabatic heat effects may be neglected because small temperature inhomogenities are compensated within 5 min. A rough estimate of the Rayleigh number in the system cyclohexane + methanol gives a value of about 900; the critical Rayleigh number for the onset of temperature equalization by convective motion is 1700 for a system with infinite rigid horizontal boundaries. It will be left up for discussion whether a Soret-driven instability whose threshold (as theory predicts [7, 8]) may be significantly smaller than that of a Rayleigh-Bénard instability is responsible for the dissipative structures.

Recently Houessou et al. [9] reported on structure formation during phase separation in an isopycnic cyclohexane + deuterated cyclohexane + methanol mixture near its critical solution point. Because of its similarity with the structures described in this work it seems necessary to accentuate the differences of experimental conditions in both cases.

- The aspect ratio of the vertical to horizontal dimensions of the cell was small for the experiments of this work but large for those of the authors cited [9]. In own test experiments with a vertical arrangement of the pressure jump cell (resulting in a large aspect ratio) no structures were formed.
- In the investigations of the authors [9] the size of the visible domains are strongly time-dependent this behaviour being interpreted as a spinodal decomposition pattern. In this work, however, the structure dimensions remain constant until the pattern thins out and finally vanishes because of coarsening mainly due to coagulation of droplets as observed microscopically.
- In contrast to the investigations of the authors [9] the mixtures used in this work were chosen off-critical (mole fraction of methanol about 0.75; temperature before pressure jump 39 °C; quench depth approximately 6 MPa). Consequently this effect has to be explained from one of the instabilities mentioned above whereas spinodal decomposition can be ruled out.

Further investigations on this phenomenon are in progress [6].

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