

Laser separation of stratifying solutions

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An optothermal separation of binary solutions with a lower critical stratification temperature has been observed in a laser beam. The effect is interpreted on the basis of a drift of particles of a disperse phase caused by gradients in the surface tension at the interfaces.

Surface phenomena in disperse systems have recently been attracting increasing research interest. Binary liquid solutions with a lower critical stratification point are examples of systems in which a disintegration and an associated formation of a textured interface occur through a phase transition during heating.¹

In this letter we are reporting experiments which have yielded the first observation of an optothermal separation of stratifying solutions during laser heating. The stratification was accompanied by a change in the absorption coefficient of the mixture during a spatial transport of its components in the field of laser light. We offer an interpretation of the effect on the basis of a photocapillary drift of particles caused by gradients of the surface tension at interfaces.

In the experiments we use the beam from an argon laser with a power ~ 1 W. As the stratifying solution we use a binary solution of water and butylcellulose, which has a lower critical stratification point of 48.3 °C. The butylcellulose concentration is 30.14% by mass and corresponds to the critical concentration. We also add to the solution an organic dye which has an intense absorption band and which is very soluble in the butylcellulose while essentially insoluble in the water. The dye concentration is $\sim 10^{-4}\%$ by mass.

To study the dynamics of the laser-induced stratification and the associated separation effect, we use photodiodes to measure the time evolution of the intensity of a probing light beam starting at the time at which the heating laser beam is turned on, as shown by the diagrams in Fig. 1 (a and b).

Figure 2a shows the time evolution found for the intensity of probing light (10 mW, $\lambda = 0.5145 \mu\text{m}$) which has passed through a liquid layer 0.2 mm thick. At time t_1 the pump light is turned on and heats the liquid. At room temperature, the liquid is a homogeneous solution. The time t_2 corresponds to the beginning of stratification and to a sharp decrease in the intensity of the probing light, because of critical opalescence. During the time interval from t_3 to t_4 , the intensity of the transmitted light in the stratified system increases because the liquid separates into a transparent phase at the center of the beam and a region of elevated dye concentration at the periphery of the beam.

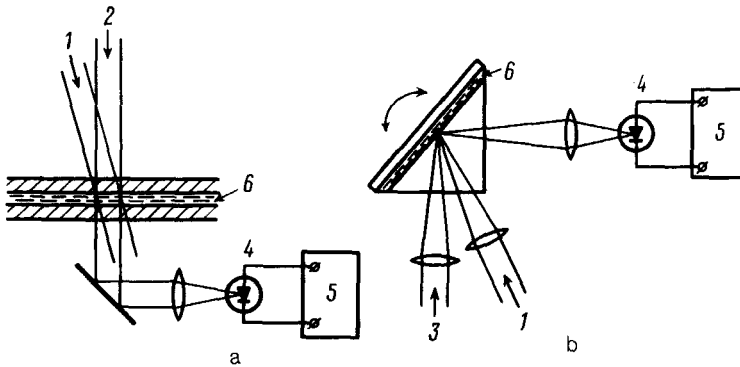


FIG. 1. Experimental arrangement. a: For a study of the dynamics of the bleaching of a solution. b: For refractometric measurements. 1,2—The pump beam and the probing beam from an argon laser; 3—probing beam from a He-Ne laser; 4—photodiode; 5—chart recorder; 6—stratifying solution.

Figure 2 shows the intensity of the light reflected from the glass-liquid interface in the arrangement of Fig. 1b. Here the intensity of the reflected light changes because of a change in the refractive index of the liquid, which tends toward the refractive index of the water as the heating proceeds. This result shows that water (with the butylcellulose admixture) collects at the center during the separation.

Our interpretation and the calculation below are based on the following facts: 1) In binary solutions with a lower stratification point, a temperature increase leads to an increase in the surface tension at the interface.² 2) A temperature gradient sets up a gradient of the surface tension and of the mass transfer near the interface through the Marangoni effect.³

Let us examine the dynamics of the mass transfer in the zone of the laser heating

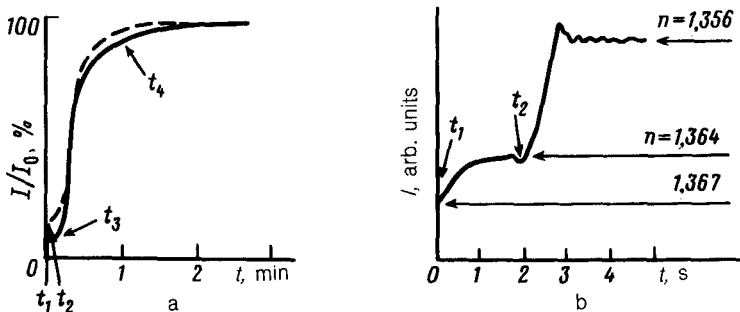


FIG. 2. a: Solid line—time evolution of the intensity of the probing beam in the experiment of Fig. 1a; dashed line—dependence calculated with $\alpha = 5 \times 10^{-11}$ and $h_1 = 10^{-4}$. b: Time evolution of the intensity of the reflected beam in the experiment of Fig. 1b. Shown at the right are the measured refractive indices of the liquid.

after the phase transition. To describe the separation effect in the initial stage of the process, we can use an expression for the velocity of a particle of the disperse phase (phase 1), of radius R , due to photophoresis⁴:

$$u_{\text{ph}} = - \frac{2\Delta\sigma}{3(3\eta_1 + 2\eta_2)} = - \frac{4R \frac{d\sigma}{dr}}{3(3\eta_1 + 2\eta_2)}, \quad (1)$$

where $d\sigma/dr$ is the gradient of the surface tension, and η_1 and η_2 are the dynamic viscosities of the disperse phase and of the dispersion medium (phase 2), respectively. Expression (1) has been derived for the case in which the volume fraction of phase 1, V_1 , is small. In the course of the separation, however, V_1 increases, and at $V_1 \sim 74\%$, corresponding to a system of close-packed spheres, expression (1) is no longer applicable. To describe the separation in this case, we consider a model of close-packed phase 1 in the form of distinct closed volumes with an average size h_1 , which are separated by unclosed intervals of phase 2 with an average size $h_2 \ll h_1$. The motion of the liquid in phases 1 and 2 obeys equations of motion written in the approximation of capillary hydrodynamics⁵ (we are assuming that motion can occur only along the coordinate r):

$$\eta_1 \frac{\partial^2 v_1}{\partial z^2} = \frac{\partial p}{\partial r}, \quad \eta_2 \frac{\partial^2 v_2}{\partial z^2} = \frac{\partial p}{\partial r} \quad (2)$$

with the boundary conditions

$$v_1|_{z=0} = v_2|_{z=0}, \quad v_1|_{z=-h_1} = v_1|_{z=0}, \quad v_2|_{z=h_2} = v_2|_{z=0}, \quad (3)$$

$$\frac{d\sigma}{dr} = \eta_1 \left. \frac{\partial v_1}{\partial z} \right|_{z=0} - \eta_2 \left. \frac{\partial v_2}{\partial z} \right|_{z=0}$$

and a continuity equation for the entire medium,

$$\int_{-h_1}^0 v_1 dz + \int_0^{h_2} v_2 dz = 0, \quad (4)$$

and one for phase 1, reflecting its closure,

$$\int_{-h_1}^0 v_1 dz = u_d h_1, \quad (5)$$

where u_d is the drift velocity of a particle of phase 1 as a whole.

Solving Eqs. (2), (4), and (5), and using (3), we find an expression for u_d

$$u_d = \frac{h_2 \frac{d\sigma}{dr}}{6(h_1 + h_2)^2} \left(\frac{h_2^2}{\eta_2} - \frac{h_1^2}{\eta_1} \right).$$

Since we worked on the basis of the model outlined above in deriving this expression, i.e., since we used $V_2 \ll V_1$, we can ignore the term h_2^2/η_2 in contrast with h_1/η_1 ,

finding as a result

$$u_d = - \frac{h_2 \frac{d\sigma}{dr}}{6\eta_1}. \quad (6)$$

The velocity of particles during photophoresis [Eq. (1)], and the drift velocity of phase 1 from (6) agree within a coefficient on the order of unity.

Since the velocity of phase 1 determines the growth rate of the transparent region at the center of the beam, we can use (6) to calculate the time dependence of the radius (r) of this region and thus the intensity of the transmitted probing beam, from the expression $I \sim 1 - \exp(-r^2/r_0^2)$, where r_0 is the radius of the probing beam. The calculated curve is the dashed curve in Fig. 2a, where the independent parameters are h_2 and the coefficient (α) in the temperature dependence of σ . Near the critical point, we approximate this dependence by the function $\sigma = \alpha(T - T_{cr})^2$.

Analysis of the experimental and calculated results leads to a conclusion regarding which of the phases in a stratifying solution should collect in the laser beam. In systems with a lower critical stratification point, the material of the dispersion medium will collect at the center; on the contrary, in systems with an upper critical point, the material of the disperse phase will collect at the center.

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Translated by Dave Parsons