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The Effect of Continuous Stirring on Off-Critical and Critical Samples of a Phase Separating Binary Liquid Mixture

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Effect of Continuous Stirring on Off-Critical and Critical Samples of a Phase-Separating Binary Liquid Mixture

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The effect of shear on phase separation in a continuously stirred mixture of isobutyric acid and water has been studied. The data for the onset of phase separation in the stirred samples that are as far away as 500 mK from the critical point compare favorably with the theory of Onuki and Takasue and with similar measurements on very off-critical mixtures of 2-6 lutidine plus water reported by Min *et al.* However, as the composition gets closer to the critical composition significant differences arise. The main feature is that the measured suppression in temperature peaks at an off-critical composition which is dependent on the stirring frequency. A simple, analytical calculation is found to show the same feature.

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Continuous vigorous stirring affects the phase-separation process in a supersaturated system. Experiments have been performed in binary fluid mixtures at both critical [1] and off-critical compositions [2]. According to the theory of Onuki and Takasue (OT) [3], for a given quench depth at a given composition there is a definite critical value of shear above which the nucleation process is totally inhibited. It can be easily understood as follows: The local shear produced by stirring ruptures the droplets down to smaller size and there is a maximum shear-dependent droplet size of radius r_{max} that can survive in the presence of shear. On the other hand, the process of nucleation has an energy barrier to be overcome to produce droplets of the minority phase. For a given quench depth there is a certain minimum critical droplet size r_c below which droplets cannot grow. Thus for shears above a critical value determined by $r_{max} = r_c$, nucleation would be totally inhibited.

The system used in the measurements reported here was a mixture of isobutyric acid and water. This system has a critical temperature $T_c = 26.18\,°C$ at a critical composition of 37.4% by volume of the acid. The critical sample and five off-critical samples with compositions $c = 30.0\%$, 32.5%, 34.9%, 36.5%, and 50.0% were prepared and sealed in sample cells made of Pyrex glass. The sample cell enclosed a Teflon-coated magnetic stirrer bar about 1 in. in length. Four vertical ribs in the inner wall of the cell help to break up the laminar circular flow of the stirred fluid and increase the level of turbulence. A temperature probe measured directly the temperature of the stirred sample. The sample cell was mounted in a water bath with a temperature control of ± 0.5 mK. The stirrer bar was magnetically coupled to a rotating horseshoe magnet outside the bath. With careful alignment of the magnet and the stirrer, stable stirring frequencies up to $f = 30$ Hz could be achieved. Light of 633-nm wavelength from a 5-mW He-Ne laser was passed through the sample and the transmitted intensity was measured with

a UDT-455HS photodiode amplifier. The measurement of the phase-separation temperature $T_{cx}(c)$ of these off-critical samples, in the absence of stirring, was done very carefully. It was important to cool in small steps and wait many hours at each step to look for the formation of a meniscus. If the cooling steps are done too rapidly, the coexistence curve can be easily overshot and the measured temperature would be at the nucleation limit, which is lower than the coexistence temperature. The measurement of $T_{cx}(c)$ was further confirmed by the alternate method of heating the phase-separated sample in small steps while gently stirring it continuously until at the temperature $T_{cx}(c)$, the transmitted intensity increased very dramatically as the components mixed to form a homogeneous mixture in the one-phase region. The samples had stabilized in the cells over a year and the measured values of $T_{cx}(c)$ were reproducible with negligible day-to-day drifts that newly prepared samples usually show. After determining $T_{cx}(c)$, the sample was heated to the one-phase region and the stirrer was turned on. The stirring causes local heating of the sample above the bath temperature. However, the thermistor monitors the actual temperature of the stirred mixture. After steady state is reached, the sample was then cooled in steps of 1 mK until at a temperature T the steady-state transmitted intensity I_F showed a dramatic fall. The important parameters recorded for each sample at each frequency of stirring were $\Delta T = T_c - T_{cx}(c)$ and $\delta T = T_{cx}(c) - T$. This was accompanied by a dramatic rise in the rms value of the temporal fluctuations in the transmitted intensity, σ. In the data shown in Table I, the two off-critical mixtures are seen to have nearly identical separation temperatures although the acid-rich mixture is much farther from the critical concentration. This asymmetry, which is more than what is usually seen in this system, is attributed to the different rates of drift of the separation temperatures since their preparation. This, however, does not affect our interpretation and analysis, since (i) the critical

TABLE I. Data for δT for samples of different compositions c for different stirring frequencies f. ΔT and ϕ are as defined in the text. The average value of $\phi/f\xi^3$ in the square brackets is $C_1' = 8.0 \times 10^{-10}$ sec$\mathring{A}^{-3}$ and of those in the curly brackets is $C_2' = 0.62 \times 10^{-10}$ sec$\mathring{A}^{-3}$. These values are used in the plots representing $\phi/f\xi^3 = C_1'$ and $\phi/f\xi^3 = C_2'$ in Fig. 3.

c (%)	ΔT (mK)	f (Hz)	δT (mK)	ϕ	$\phi/f\xi^3$ (10^{10} sec$\mathring{A}^{-3}$)
30.0	530	10	19	0.0057	[9.2]
		20	31	0.0092	[7.7]
		30	38	0.0112	[6.3]
32.5	203	10	18	0.0137	4.1
		20	29	0.0214	3.5
		30	50	0.0348	4.4
34.9	62	10	25	0.0526	2.8
		20	39	0.0739	2.7
		30	51	0.0894	2.6
36.6	16	10	10	0.0736	0.43
		20	25	0.1328	0.87
		30	26	0.1357	0.67
37.4 (c_c)	0	10	10	0.5	{0.53}
		20	17	0.5	{0.67}
		30	21	0.5	{0.67}
50.0	524	10	17	0.0052	[8.2]
		20	35	0.0105	[8.7]
		30	45	0.0133	[7.7]

sample still shows the highest separation temperature and the meniscus forms at the center of the cell when kept a few millikelvin below T_c, and (ii) the relevant parameter $\Delta T = T_c - T_{cx}(c)$ has been carefully measured for each sample.

Figures 1(a) and 1(b) show the fall in I_F and the corresponding rise in σ for two samples, one far away and one close to the critical composition, respectively. It can be seen that the transition is very sharp for off-critical samples and the corresponding suppression δT could be determined to well within a millikelvin. For samples very close to critical, though the transition is not as sharp δT could be determined to within ± 2 mK in the worst case. The results are listed in Table I.

A brief review of the theory of OT for the suppression of nucleation by shear will help interpret the data. As discussed earlier, for a given shear S the suppression δT is determined by the limiting condition $r_{max} = r_c$. The critical radius is $r_c \approx \xi/\phi$, where ξ is the correlation length and ϕ is the volume fraction of the minority phase. ϕ can be calculated for a given ΔT and δT by $\phi = \frac{1}{2} - \frac{1}{2}(1 + \delta T/\Delta T)^{-\beta}$, where β is the exponent corresponding to the coexistence curve $= 0.328$ [4]. $r_{max} = C\sigma/\eta S$, where σ is the surface tension given by $\sigma = 0.1 k_B T/\xi^2$ near the critical point [5], η is the fluid viscosity, k_B is the Boltzmann constant, and C is a constant weakly dependent on the type of flow [6]. Thus the condition $r_{max} = r_c$ becomes
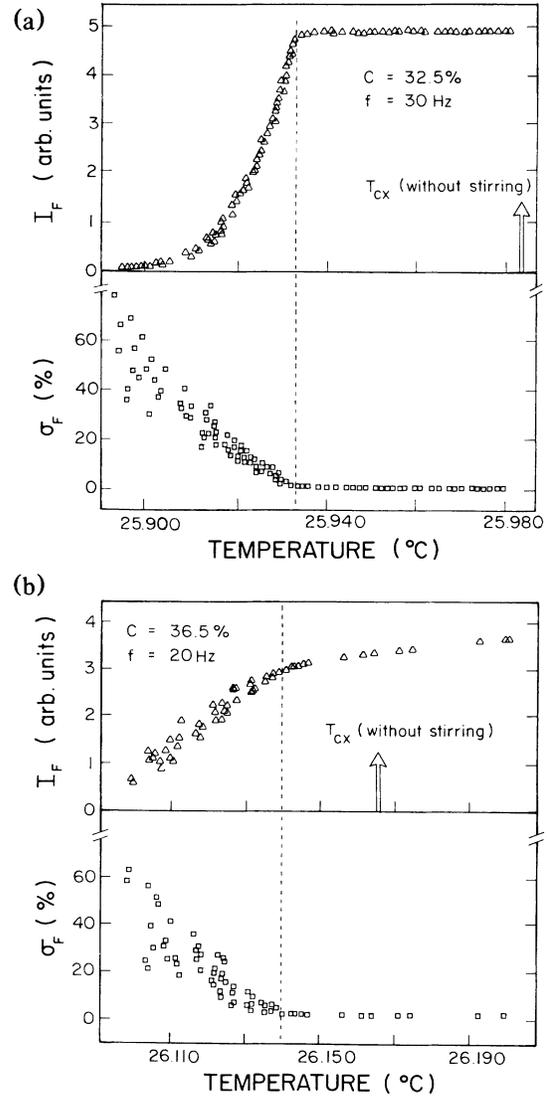
$$\phi/S\xi^3 = \text{const} = C_1 \qquad (1)$$

FIG. 1. (a) The steady-state transmitted intensity I_F and the rms value of the fluctuations in the transmitted intensity σ_F plotted as a function of temperature as the stirred sample ($c = 32.5\%$, $f = 30$ Hz) is cooled in steps. The unstirred phase-separation temperature T_{cx} is represented by the arrow on the temperature axis. (b) The steady-state transmitted intensity I_F and the rms value of the fluctuations in the transmitted intensity σ_F plotted as a function of temperature as the stirred sample ($c = 36.5\%$, $f = 20$ Hz) is cooled in steps. The unstirred phase-separation temperature T_{cx} is represented by the arrow on the temperature axis.

for off-critical samples.

For the sample at the critical composition, there is no energy barrier for the formation of critical droplets and the system directly enters the spinodal region on quenching below T_c. In this case the suppression is determined by the condition that the inverse lifetime of the composition fluctuations of length scale ξ given by $\Gamma = k_B T/6\pi\eta\xi^3$ equals the shear rate S. At the critical composi-

tion, taking $\phi = 0.5$ for all quenches, the above condition is equivalent to

$$\phi/S\xi^3 = \text{const} = C_2 \tag{2}$$

for the critical sample. ξ is calculated as $\xi_0^-[(\Delta T + \delta T)/T_c]^{-\nu}$ with $\xi_0^- = 1.8$ Å and $\nu = 0.613$. Comparison of the data with the above models and the interpretation are done in three different segments of the coexistence curve.

(i) *Samples with* $\Delta T \gg \delta T$.— The two samples at $c = 30.0\%$ and 50.0% are ≈ 500 mK away from T_c on either side of the coexistence curve. For these samples $\phi/f\xi^3$ is found to be a constant in agreement with the predictions of OT. It should be noted that $\phi/f^{3/2}\xi^3$ is not a constant, consistent with laminar shear ($S \propto f$) rather than turbulent shear ($S \propto f^{3/2}$) in the cell. The above results are entirely consistent with those from the data on 2-6 luditine plus water system reported by Min *et al.* [2].

(ii) *The sample at the critical composition.*— For this sample, $\phi/f\xi^3$ is found to be a constant different from the constant in (i). The measurements give

$$[\phi/f\xi^3]_{\Delta T \gg \delta T} = [12 \pm 3][\phi/f\xi^3]_{T=T_c}. \tag{3}$$

The above can be compared to what is expected from Eqs. (1) and (2). From the discussions leading to Eqs. (1) and (2) the value of $C_1/C_2 = (0.3\pi C)^{-1}$. The value of C, as discussed earlier, is weakly dependent on the type of flow. The construction and detail of the sample cell and stirring setup used here is similar to that used by Min *et al.* [2] who reported a value of $C = 0.16 \pm 0.05$ (in agreement with published values [6]) obtained from their extensive data on 2-6 lutidine plus water. Using this value of C, the expected range for C_1/C_2 is 5.1 to 9.6.
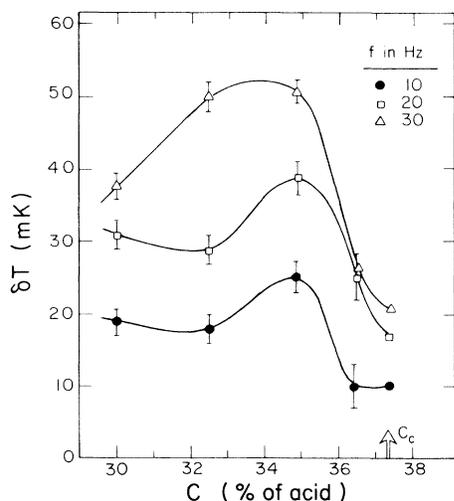
The value of 12 ± 3 for C_1/C_2 obtained from the data represented by Eq. (3) does seem reasonable. It should be noted that the viscosity varies by about 17% over the range of concentrations studied [7]. This is small compared to the observed variation of $\phi/f\xi^3$.

(iii) *Intermediate samples.*— For these samples, as seen in Table I, the value of $\phi/f\xi^3$ is continuously varying between the constant values at $T = T_c$ and $\Delta T \gg \delta T$. This feature can be interpreted as a gradual transition from the model for the situation at $T = T_c$ to the model for $\Delta T \gg \delta T$. It is important to note that the system is far from equilibrium with $\Delta T \approx \delta T$ and it is not clear that the expression used to calculate ξ is correct for the situation. However, the interesting feature that emerges from the measurements is that there is an increase in δT at fixed frequency as we go away from the critical composition, peaking at some off-critical composition. This feature is seen at each frequency. At higher frequencies the off-critical composition at which δT peaks shifts farther away from c_c. All these features can be seen in Fig. 2 which is a plot of the experimental data. Let us look for a moment at the equation $\phi/f\xi^3 = \text{const}$ and ignore
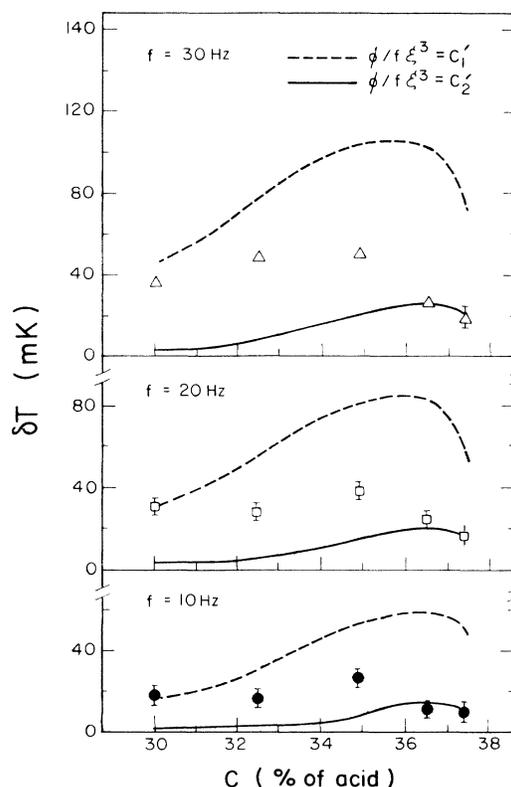

FIG. 3. Data for $f = 10$, 20, and 30 Hz superposed on the curves representing $\phi/f\xi^3 = C_1'$ (dotted) and $\phi/f\xi^3 = C_2'$ (solid). The values of C_1' and C_2' chosen for the curves are the average of the measured values (see Table I) given by $C_1' = 8.0 \times 10^{-10}$ sec Å^{-3} (average of the values indicated by the square brackets in Table I) and $C_2' = 0.62 \times 10^{-10}$ sec Å^{-3} (average of the values indicated by the curly brackets in Table I).

FIG. 2. Plot of δT for samples of different compositions, for stirring frequencies $f = 10$, 20, and 30 Hz. The error bars for the data at $c = c_c$ are comparable to those indicated for $c = 36.5\%$.

the fact that the value of the constant slowly changes as the sample becomes more off critical. The analytic solution for δT which keeps $\phi/f\xi^3 =$ const also reveals a peak in δT, as seen in Fig. 3. Figure 3 shows the curves for δT which are solutions for $\phi/f\xi^3 = C_1'$ and $\phi/f\xi^3 = C_2'$ superposed on the data for each frequency. C_1' and C_2' are measured values (see Table I). As expected the data lie between the curves.

In conclusion, the measurements of the suppression of nucleation in stirred binary liquid mixtures seem to be well explained by the model of Onuki and Takasue. The data for samples far from T_c and those at T_c satisfy $\phi/f\xi^3 =$ const, with different values of the constant for each of the two situations. It is interesting to see that a simple analytical solution to $\phi/f\xi^3 =$ const also reveals the peak in the suppression at off-critical compositions as seen in the data. The position of the peak is seen to be dependent on the value of the constant.

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