A Videographic Study of Dynamic Phase Separation for Immiscible Solutions under Acoustic Levitation Condition *

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The transparent aqueous solutions of succinonitrile (SCN) provide an effective model system to simulate the phase separation process of various advanced materials. Here we report a real-time and in-situ study of phase separation dynamics for the SCN-15%H_2O, SCN-48%H_2O and SCN-70%H_2O solutions implemented by high-speed CCD videography together with acoustic levitation technique. It is found that liquid phase separation induces an unsteady state of drop rotation under levitated conditions. The resultant centrifugal force plays the dominant role in the migration of secondary liquid globules. The most desirable homogeneously dispersive structures can only be derived from the earlier stage of phase separation, whereas three kinds of macrosegregation are always the finally stable structure patterns. The migration velocity of minor liquid phase displays the nonlinear feature owing to the variations of globule location and centrifugal force. The surface tensions and volume fractions of immiscible phases also show a conspicuous influence upon the evolution dynamics of separation morphology.

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Phase separation is an important physical phenomenon occurring in various advanced materials such as metallic alloys,[1,2] inorganic systems[3,4] and macromolecular polymers.[5,6] The modulation of this phase transformation may be applied as an efficient approach to optimize and control expected structures during materials fabrication and processing. For instance, homogeneous dispersion microstructures are usually anticipated from rapid solidification of monotectic-type alloys, while the symmetrical core-shell structures are quite popular during the synthesis of inorganic and polymetric materials. Meanwhile, the physical mechanisms of secondary liquid nucleation, Stokes motion and Marangoni migration are of evident significance for fundamental research.[7–9] In particular, this is also an interesting subject for microgravity study in the field of space science and technology. Although there has been extensive work about phase separation in both experimental research and numerical simulations,[10,11] the usual opaque nature of most materials hinders the implementation of real-time and in-situ observations on the phase separation dynamics.

Acoustic levitation has the advantage of suspending nonconductive materials even aqueous solutions.[12,13] It supplies a suitable way to simulate the microgravity and containerless states of outer space environment. When a drop of solution is acoustically levitated, it usually rotates and oscillates according to the different orders of resonant modes.[14,15] Despite the numerous investigations about the axisymmetric oscillation, multiple-lobed bifurcation and internal flow pattern of levitated liquid drops,[16–20] the experimental attempts towards the liquid phase separation under acoustic levitation is less frequently reported. The objective of this work is to accomplish a real-time and in-situ study of dynamic phase separation by combining high-speed CCD videography with acoustic levitation technique. The transparent SCN-H_2O solutions are chosen as a model immiscible system. Special attention is directed to the evolution dynamics of homogeneous composites and core-shell structures.

The experiments were carried out with a single-axis acoustic levitator[12] at a frequency of 16.7 kHz. SCN-H_2O solutions form a typical immiscible system, in which liquid phase separation takes place when the H_2O content is in the range of 8.9–89.1 wt.%. Because the 0.998 g/cm^3 density of SCN is very close to that of H_2O, the convection and deposition phenomena induced by density difference are weakened during the experiment. On the other hand, the immiscible temperature of 329.03 K in SCN-H_2O phase diagram is slightly higher than the room temperature, which provides convenience to control the experimental temperature and observe the phase separation process. The phenolphthalein-NaOH was used as the tracer to make the H_2O dyed red, which could be distinguished by colors in the experiment, as shown in Fig. 1(c). Three compositions of SCN-15%H_2O, SCN-48%H_2O, and SCN-70%H_2O solutions were selected to investigate the phase separation process. The volume fractions of solute component are 7.8%H_2O, 48.8%H_2O and 23.3%SCN, respectively, according to the phase diagram, as seen in Fig. 1(a). The initially homogeneous solution was prepared by an alcohol blast burner inside beaker, then it was injected into the acoustic pressure node with a syringe to realize levitation, then cooled directly in the air to room temperature. The process of phase separation was recorded by a high speed CCD camera of Redlake HG 100 K type at 60 fps

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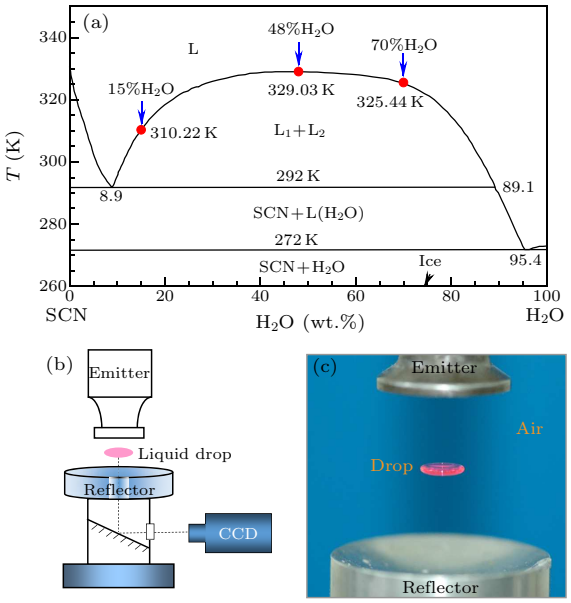

Fig. 1. Experimental design of dynamic phase separation: (a) selected aqueous solutions in SCN-H_2O phase diagram, (b) acoustic levitator, and (c) experimental process.

The SCN-15%H_2O, SCN-48%H_2O, and SCN-70%H_2O solutions are located in the immiscible zone (seen in Fig. 1(a)) and liquid phase separation will take place once the temperature is cooled into the miscibility gap. The previous homogeneous drop separates into two immiscible liquid phases in the process of experiment. The phase separation process and rotation time were recorded by the high speed CCD camera from a small window at the reflector center, as seen in Fig. 1(b). The levitated drop was pressed into a little pie with the size of $\phi 6 \times 2$ mm and rotated slowly with first-order motion due to the effect of acoustic radiation pressure during the experiment, as shown in Fig. 1(c).

Figure 2 shows the structure patterns for three kinds of SCN-H_2O solutions under acoustic levitation. When the H_2O content is only 15% in the SCN-H_2O solution, the microstructure displays the dispersed pattern, where the liquid H_2O phase distributes dispersedly into the SCN solvent matrix at the beginning of phase separation, as shown in Fig. 2(a1). Here the volume fraction of H_2O phase occupies 7.8% of the levitated drop, meanwhile a thin layer of H_2O film is formed at the drop edge. With the extension of levitation time, the H_2O globules migrate gradually outwards to the periphery of the levitated drop, and the peripheral macrosegregation structure is finally formed, which is characterized by the SCN solvent surrounded by the H_2O solute layer (see Fig. 2(a5)).

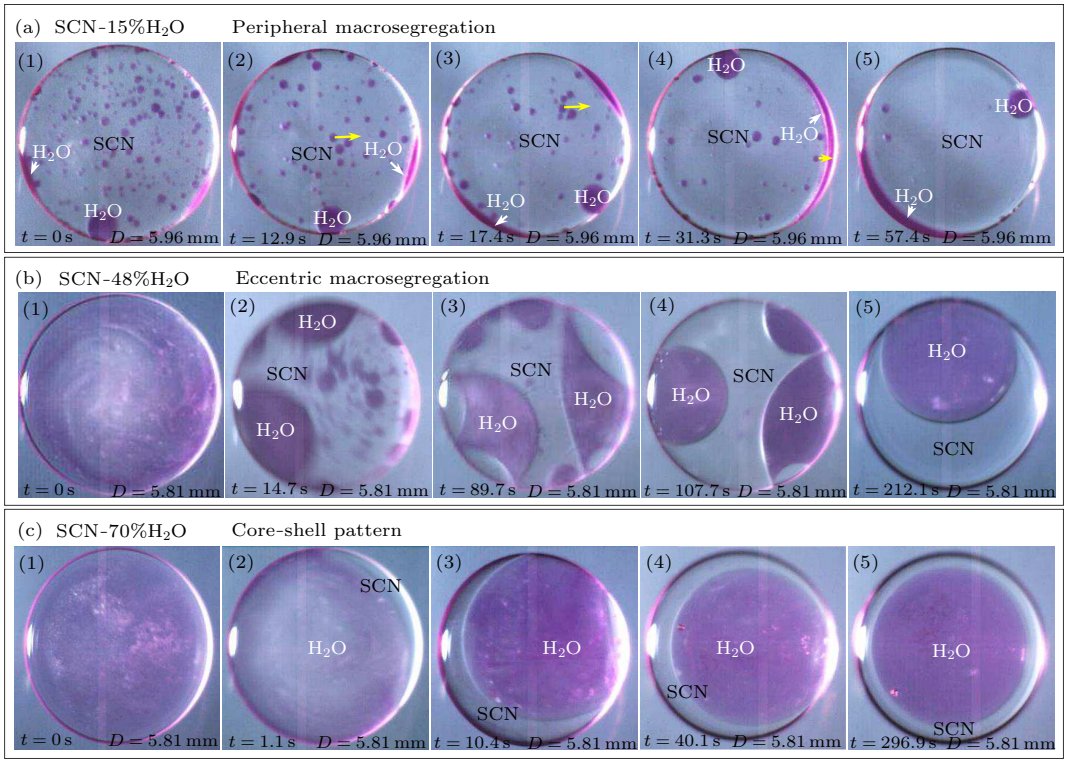

Fig. 2. Phase separation processes of three aqueous solutions under the acoustic levitation condition: (a) SCN-15% H_2O, (b) SCN-48% H_2O, and (c) SCN-70% H_2O.

Once the H_2O content attains 48% in SCN-H_2O solution, where the volume fraction of H_2O solute is 48.8%, the levitated drop will display the homogeneous characteristics at the beginning of phase separation, and even the rotation ripple can be seen in Fig. 2 (b1) simultaneously. Then the phase separation occurs with the extension of levitation time. When the levitation time t=14.7 s, the H_2O solute aggregates together under the effect of hydrodynamic and centrifugal forces generated by rotational action, and forms the large and nubby globules near the edge of the SCN-48%H_2O drop, as shown in Fig. 2 (b2) and (b3). When the levitation time extends to 212.2 s, the H_2O solute aggregates completely and results in the two-layer eccentric macrosegregation structure, as seen in Fig. 2 (b5). Similarly, when the H_2O content increases to 70% and the volume fraction of SCN solute attains 23.3%, the SCN-H_2O solution displays the homogenous structure before the phase separation (see Fig. 2 (c1)). Once phase separation occurs, the minor phase of SCN solute will migrate outwards under the effects of hydrodynamics, acoustic radiation pressure and centrifugal force and will form the macrosegregation layer, as illustrated in Fig. 2 (c2). The macrosegregation layer thickens gradually with the extension of levitation time and the liquid H_2O solvent moves towards the droplet center. Ultimately, the symmetrical core-shell structure forms under acoustic levitation, as shown in Fig. 2(c5).

The microstructure of the SCN-H_2O solution mainly depends on the rotating speed under the effect of acoustic radiation pressure, which accelerates the second globules to move outside. The drop begins to rotate under acoustic radiation pressure once it is injected into the pressure node by syringe to realize levitation, here the rotational motion is the first-order oscillation.[13,14] However, the rotating speed of levitated drop is unstable with the extension of levitation time, it is related to the segregation degree of the surface layer and globules size on the drop edge. For example, the rotating speed increases from ω =0.66 rad/s at t=10.3 s to ω =0.91 rad/s at t=20.4 s for the SCN-15%H_2O solution, then it decreases rapidly to only 0.46 rad/s at t=54.7 s, because the H_2O layer at the drop edge presents asymmetric characteristics, as demonstrated in Fig. 3(a). Subsequently it increases gradually in the stepped way with the extension of levitation time, which depends on the surface layer distribution. However, the rotating speed reduces rapidly from ω =2.73 rad/s at t=3.3 s to ω =1.91 rad/s at t=49.0 s for the SCN-48%H_2O solution, and the oscillation character appears with the extension of levitation time, as illustrated in Fig. 3(b). The reason is that the phase separation takes place with the extension of levitation time and the decrease of temperature, the larger globules aggregate together at the drop edge under the effects of hydrodynamics and rotational action, thus the rotating speed loses its balance. Then it grows increasingly and the maximum value attains 2.64 rad/s at t=107.7 s. As the nubby H_2O solutes distribute at different positions near the drop edge, they are relatively symmetrical, and the rotating speed is also relatively stable. Afterwards it declines with the extension of levitation time, and two inflection points display at 139.8 and 165.2 s, respectively, since the nubby H_2O solutes collide and coagulate under the effect of rotational action. Finally the macrosegregation structure forms at t=212.1 s, where the rotating speed ω=2.05 rad/s. For the SCN-70%H_2O solution, the rotating speed rises rapidly when the levitation time is smaller than 24.2 s. Since the liquid solution displays the homogeneous feature although the phase separation takes place at t=1.1 s, the SCN solute migrates outwards the drop edge and presents the crescent shape SCN zone, which has little influence on the rotating speed, as illustrated in Fig. 3(c). The maximum value of rotating speed 2.02 rad/s appears at t=24.2 s, which may demonstrate that the migration of SCN solute is finished in the liquid solution, and forms the eccentric core-shell structure. Afterwards the rotating speed decreases with the extension of levitation time, and two inflection points occur at 161.9 and 196.7 s, where the rotating speeds are 0.93 and 1.09 rad/s, respectively. This demonstrates that the H_2O solvent moves towards the drop center under the effect of rotational action and forms core-shell structure. Therefore the microstructure also has some influence on the rotating speed during acoustic levitation.

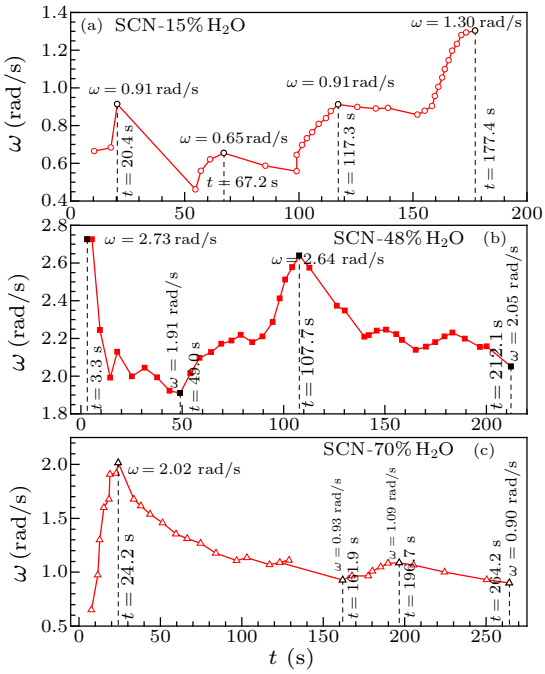

Fig. 3. Drop rotating speeds of three aqueous solutions at acoustically levitated state: (a) SCN-15% H_2O, (b) SCN-48% H_2O, and (c) SCN-70% H_2O.

There are at last six forces acted on a levitated drop under acoustic levitation: buoyancy, gravity, centrifugal force, Marangoni migration force, friction, and

acoustic radiation pressure, respectively. The centrifugal force has the significant influence on the migrating process of the globules of minor liquid phase for the immiscible solution under the acoustic levitation condition, which is produced by the rotational process of acoustic radiation pressure. The buoyance and gravity offset each other in the process of the levitation experiment. The friction can be neglected because it has rather small effect. Although there has the Marangoni migration force exerting on the globules, it has the smaller influence on the globules than the centrifugal force. An SCN-H_2O drop is pressed into a little pie by the acoustic radiation pressure and yields the rotational effect during the experiment, whereas it has the smaller effect on the phase separation process of the immiscible solution than the centrifugal force. Therefore, the centrifugal force is considered as the dominant factor in this work, and it is described as a ratio to the gravity of a migrating globule by the equation

$$f_r = \omega^2 r/g, \tag{1}$$

where ω is the angular speed, r is the distance from drop center to the globule location, g is the gravitational acceleration and R represents drop radius. From Fig. 4 we can see that the globules near the drop edge experience 4 times larger centrifugal force than those at the drop center. For example, the reduced centrifugal force f_r in the SCN-15%H_2O solution for r=2.8 mm is 0.24 at levitation time t=20.4 s, which is only 0.06 for r=0.7 mm. Meanwhile the 72 dyne/cm surface tension of H_2O is larger than that of 42.6 dyne/cm for SCN, the volume fraction of H_2O phase occupies 7.8% of the levitated drop, thus the large H_2O globules near the drop edge move rapidly outwards and form a thin layer of H_2O film, as seen in Fig. 4(a). The inner globules also migrate towards the drop edge under the effects of the volume fraction, surface tension and centrifugal force. The closer to the drop, the larger the centrifugal force. There is a large centrifugal force at the beginning of levitation and phase separation process for the SCN-48%H_2O solution in Fig. 4(b). Then the centrifugal force decreases with the levitation time, meanwhile the centrifugal force curve has the oscillation character before t=107.7 s, those near the drop edge are more obvious than that of the inner drop. It is clear that a large number of H_2O globules move towards to the drop edge under the effects of the volume fraction, surface tension and centrifugal force, they experience the processes of collision, coagulation and Ostwald ripening and form the large H_2O globules at the drop edge. Thereafter the centrifugal force decreases with the levitation time and two inflection points appear at 139.8 and 164.2 s, respectively, which demonstrates that the large globules seen in Fig. 2(b4) exhibit the process of collision and coagulation, finally it forms the macrosegregation structure. In addition, the centrifugal force of the SCN-70%H_2O solution increases rapidly before t=24.2 s with the extension of levitation time, indicating that SCN globules of the smaller surface tension migrate outwards the drop rapidly because of the smaller volume fraction, at the same time the SCN globules near the drop edge move quickly than the inner SCN globules under the effects of the volume fraction and centrifugal force, as shown in Fig. 4(c), the SCN-70%H_2O drop forms the asymmetric macrosegregation structure so that the H_2O solvent is surrounded by the SCN solute. With the extension of levitation time, the centrifugal force declines gradually and an obvious inflection point displays at t=161.9 s, indicating that the outer layer SCN solute distributes homogeneously and forms the core-shell structure that the H_2O core is surrounded by SCN shell. Therefore, the volume fraction, surface tension and centrifugal force have the significant influence on the final structure of the SCN-H_2O solution under the acoustic levitation condition.

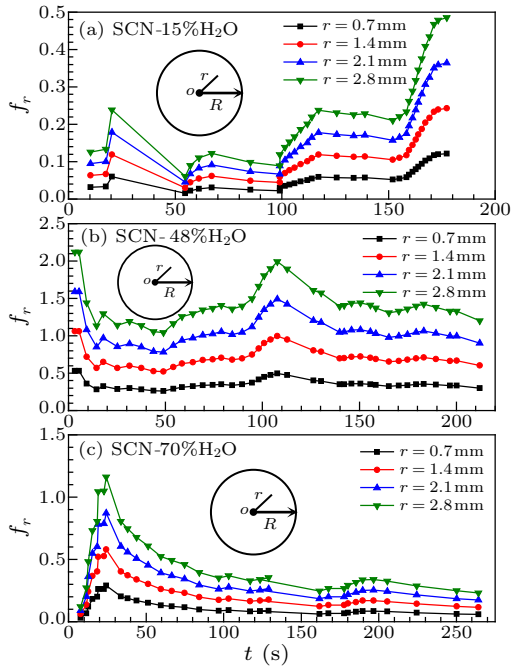

Fig. 4. Centrifugal forces at different positions inside acoustically levitated drops versus evolution time: (a) SCN-15% H_2O, (b) SCN-48% H_2O, and (c) SCN-70% H_2O.

The rotational speed and centrifugal force have the significant influences on the migration velocity of the minor phase under the acoustic levitation. However, the migration velocity can not be measured for the SCN-48%H_2O and SCN-70%H_2O solutions during the experiment owing to the higher solute contents. Therefore, the migration velocity of the H_2O globule for SCN-15%H_2O was measured in the experiment, the selected globule is marked in Fig. 2(a) and the measured result is illustrated in Fig. 5. The migration velocity V_m is 40.6 μm/s at t=7.2 s. The migration velocity increases with the extension of levitation time, its values are 84.5, 86.8 and 87.9 μm/s at 17.4, 23.4 and 31.2 s, respectively. Then the migration velocity decreases with the levitation time and the value is

72.0 μm/s at 41.1 s. Clearly, the H_2O globule near the drop center has the small centrifugal force. With the extension of levitation time, the H_2O globule moves outwards to the drop under the effect of rotational action and centrifugal force. When the levitation time t is larger than 17.4 s, the migration velocity increases rapidly due to the H_2O globule moves to near the droplet edge where the centrifugal force remarkably enhances according to the calculated result in Fig. 4(a). The migration velocity decreases at t>31.2 s since the H_2O globule is nearest the drop edge, then it is coagulated by the H_2O shell layer. Clearly, the migration velocity is closely related to the rotating speed and centrifugal force.

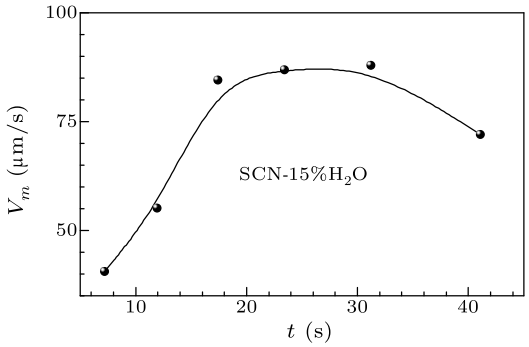

Fig. 5. The migration velocity of H_2O globules within the acoustically levitated SCN-15%H_2O droplet.

In summary, the transparent SCN-H_2O solutions are used as a model system to explore the dynamic process of phase separation, which frequently happens in various advanced materials. The real-time and in-situ observations were performed by combining high-speed CCD videography with acoustic levitation technique. The floating drop is immediately pressed into a little pie as soon as aqueous SCN solution has been injected to acoustic field. It begins to rotate under the effect of first-order oscillation. Owing to the initiation of liquid phase separation, it transforms from a homogeneous single-phase solution into a mixture of two immiscible liquid phases. The unsteady state of drop rotation provides an apparent indication for the progress of liquid phase separation. Disregarding the volume fraction of the minor secondary liquid phase, the videographic study reveals that the uniform dispersion pattern only appears at the initial stage of phase separation and remains merely for a short period of time. The centrifugal force resulting from the unsteady rotation of acoustically levitated drop exhibits a dominant role upon the migration of minor phase globules. Three kinds of stable structure morphologies are produced finally: the peripheral macrosegregation for SCN-15%H_2O solution, the eccentric macrosegregation of SCN-48%H_2O solution, and the core-shell pattern for SCN-70%H_2O solution. Both the volume fraction and surface tension of the separated liquid phases show a certain effect on the evolution of final segregation patterns.

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