Entropy Driven Phase Separation in Binary Emulsions

Ullrich Steiner, Amit Meller, and Joel Stavans

Department of Complex Systems, Weizmann Institute of Science, Rehovot 76100, Israel

(Received 29 December 1994)

We have studied experimentally phase separation in binary mixtures comprised of nearly monodisperse emulsion droplets of two different sizes. For three values of ξ, where $\xi < 1$ is the size ratio, we have determined phase diagrams and find that segregation occurs for $\xi \leq 0.30 \pm 0.02$. The phase boundaries are strongly dependent on ξ, and phase-separated samples show nearly complete segregation of the two components, as a result of the *osmotic depletion* effect which drives the phase segregation. Our results agree qualitatively with recent model calculations.

PACS numbers: 82.70.Kj, 64.70.–p, 64.75.+g

Phase separation in binary fluid mixtures is a widely studied problem in statistical mechanics. Usually, the segregation of a mixture into different phases originates from the competition of the enthalpic and entropic contributes to the free energy. Evidence supporting this picture was provided by the analytical calculations of Lebowitz and Rowlinson [1,2] over thirty years ago. They predicted that a binary mixture of hard spheres of two different sizes is miscible for all concentrations and size ratios. Biben and Hansen [3] have recently contested this notion. Using a different closure of the Ornstein-Zernike equation, they suggest that binary hard sphere mixtures indeed phase separate, provided the sizes of the constituents are different enough. Their conclusions have more recently been supported by density functional theory calculations [4] as well as computer simulations [5]. The physical origin of phase separation in hard sphere mixtures is the *osmotic depletion effect* [6,7]: when two large spheres approach each other, the small spheres are expelled from the closing gap, leading to an uncompensated osmotic pressure difference between the gap and the outer surfaces. This induces an effective attraction between the large spheres, despite the fact that there are no attractive enthalpic interactions [8]. Hard sphere systems are a purely theoretical model and do not exist in nature. Nonetheless, attractive *depletion interactions* may be dominant in mixtures consisting of two species of sufficiently compact objects whose enthalpic interactions are very weak. In fact, depletion interactions are responsible for the micelle-induced creaming of emulsions [9], phase separation observed in heterogeneous systems such as colloid-polymer [10–12] and colloid-surfactant [13] mixtures, and the enhanced reaction rates of macromolecules in the crowded cytoplasm of a biological cell [14].

Several experimental studies of depletion-induced phase separation have been performed mainly in heterogeneous systems such as polymer-colloid suspensions [10,11,15,16]. While the results agree qualitatively with models specifically tailored for these systems, there are no systematic studies of the phase behavior of mixtures in which small and large particles have the same identity, as a function of the size ratio. Existing investigations purporting to mimic hard spheres have reported phase diagrams of a single value of the size ratio and very small values of this parameter [15,16]. In this Letter we present a study of a novel system which overcomes these limitations: emulsions comprised of droplets of two different sizes. The interactions between the spherical oil droplets of our emulsions are very weak and of short range, and they exhibit only small shape fluctuations [17]. This makes our emulsions suitable approximations to a hard-core fluid. This system allows us to explore a large range of the size ratios ξ ($\xi = r_{\mathrm{small}}/r_{\mathrm{large}}$ where r is the droplet radius) and, in particular, the interesting regime near $\xi = 0.25$, above which no phase separation is predicted to occur [3].

Raw stock emulsions were prepared from water, silicon oil, and sodium dodecyl sulfate (SDS) using the classical inversion method [18], employing a conventional stirrer. The large oil drops (~ 10 μm) were then broken up using a high speed dispersion tool. Nearly monodisperse emulsions were prepared by 6–8 successive fractionations [9]. Emulsions with the smallest drop sizes ($r < 0.5$ μm) were concentrated by centrifugation for several hours at 10 000 g. The resulting fractions were analyzed by dynamic light scattering to determine the droplet diameter and polydispersity. Oil concentrations were determined by weighing a small quantity of the emulsion before and after evaporation of the water in a drying oven ($T \approx 60$ °C). The final stock emulsions from which the binary mixtures were prepared were dialyzed against a bath containing 2.3 g/l SDS corresponding to one critical micelle concentration (CMC). A concentration of 1 CMC SDS was maintained in the aqueous phase throughout our experiments.

The characteristics of the five stock emulsions are summarized in Table I. From these, mixtures of three different size ratios ξ were prepared: D/A, $\xi = 0.09$; D/B, $\xi = 0.13$; and E/C, $\xi = 0.29$. The density (at $T = 20$ °C) of the oil in emulsions A,B,C (D,E) is 0.937 g/cm^3 (0.920 g/cm^3). To detect phase separation (all samples are milky white in their native state due to multiple light

Sample	Drop diameter[a] (nm)	Polydispersity[a] (%)	Refractive index[b]
A	2635 ± 100	12	1.4022
B	1635 ± 50	7	1.4022
C	885 ± 15	6	1.4022
D	224 ± 5	10	1.3984
E	259 ± 5	10	1.3984

[a] Determined by dynamic light scattering.
[b] At 25 °C.

scattering from the oil droplets), we added urea to the stock emulsions in order to match the refractive index of the aqueous phase to that of the oil used in emulsions D and E. While the required amount of urea (42.74% of the aqueous phase at 25 °C) renders samples D and E completely transparent, it leaves emulsions A, B, and C slightly opaque, due to the higher refractive index of the oil used in these emulsions, thus allowing one to distinguish phases of different composition. All experiments were carried out at room temperature ($T \approx 25$ °C).

Phase coexistence curves were measured using two complementary techniques. In a first procedure, a series of samples of constant volume fraction of large spheres ϕ_ℓ and varying concentration of small spheres ϕ_s were prepared and mixed. Each sample series was observed visually and recorded by time-lapse video for periods up to several days. For overall volume fractions $\phi < 0.5$, we have observed rapid phase separation of the samples for all three size ratios as soon as ϕ_s exceeds a critical value $\phi_s^{\text{crit}}(\phi_\ell)$. The typical time scales for the phase separation process ranged from a few minutes to several hours, depending on the size ratio and total volume fraction. In a representative sample series ($\phi_\ell = \text{const}$), all samples with $\phi_s < \phi_s^{\text{crit}}$ stayed homogeneous over similar time scales as a monocomponent reference sample, whereas samples with $\phi_s > \phi_s^{\text{crit}}$ rapidly separated into a turbid upper phase and a clear lower phase. We identify the points $(\phi_\ell, \phi_s^{\text{crit}})$ as the phase boundary.

In a second experimental procedure, we examined samples of compositions ϕ_ℓ and ϕ_s which lie in the two phase region. After the two phases have equilibrated following the phase separation as discussed above, we analyzed the composition of two coexisting phases. The analysis takes into account the following consideration: Any sample, stable or not, shows over time the formation of a supernatant cream due to the buoyancy of the oil drops. Gravity also induces an additional compression of the upper phase of unstable samples, thereby increasing the volume fraction. It is therefore necessary to achieve a clear separation of time scales between creaming induced by phase separation and that induced by buoyancy alone. This was accomplished by choosing emulsions with small droplet radii. In the present experiments, the characteristic time for buoyancy-induced creaming is approximately one order of magnitude higher than the time scale of phase separation. For sample analysis, we monitored the phase separation process with time, and compared it to samples which exhibit purely gravitational creaming. In Fig. 1 we plot the position of the interface between the cream and the suspension (measured from the bottom of the sample) versus time, obtained using a computerized image analysis system [19]. For the sample with $\phi_\ell = 0.10$, $\phi_s = 0.14$ ($\xi = 0.09$), initial rapid segregation ($\tau \approx 15$ min) is followed by a slower relaxation process. The compositions of the two phases were analyzed when the interface position was within (2–3)% from its equilibrium value (arrow). In a reference sample of the same overall oil concentration ($\phi_\ell = 0.24$, $\phi_s = 0$), gravitational creaming led to a much smaller effect, and we believe the contribution of gravitational creaming is of minor significance in the present experiment [20]. In all the samples which exhibit phase segregation, we observe segregation of the small spheres, and only small concentrations ϕ_s remain in the upper phase at equilibrium. In some cases the upper phase exhibits iridescence, indicating a crystalline structure, while in others, the upper (solid) phase seems to be amorphous. This is currently under investigation. For the size ratios $\xi = 0.09$ and $\xi = 0.13$, the lower phase is transparent after phase separation, indicating that $\phi_\ell < 0.01$ for samples which lie sufficiently far from the phase boundary. In these cases, the assumption $\phi_\ell \approx 0$ in the lower phase greatly facilitates the task of determining the composition of both fractions, and knowing the composition of the sample before phase separation only the overall oil concentration of the two phases is needed to deduce the composition (ϕ_ℓ, ϕ_s) of both phases with sufficient accuracy. This approach also provides data about the right branch ($\phi_\ell > 0.55$) of the coexistence curve, which cannot be obtained by the first method. While the assumption $\phi_\ell = 0$ for the lower

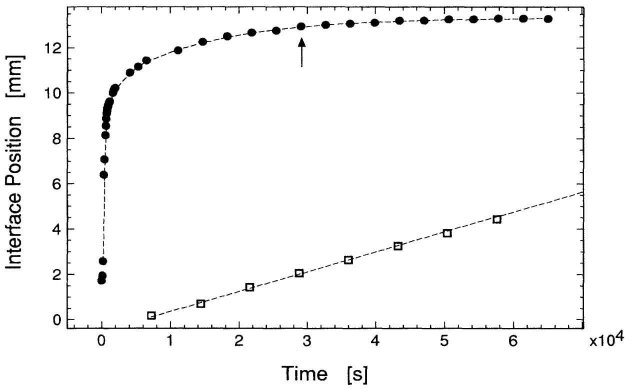

FIG. 1. Movement of the interface separating two phases during the creaming of an emulsion. The solid circles show a sample undergoing creaming induced by phase segregation for a sample with $\xi = 0.09$, $\phi_\ell = 0.1$, and $\phi_s = 0.14$. The control sample ($\phi_\ell = 0.24$, $\phi_s = 0$) exhibits gravitational creaming, which proceeds more slowly. The arrow indicates a time close to equilibrium when the sample was analyzed (see text).

phase is not justifiable in the case where $\xi = 0.29$, an alternative approach which involves a second fractionation of the two phases is currently explored [19].

The combined results of all our measurements yield the phase diagrams of Fig. 2, the central result of this paper. The solid triangles indicate the samples which undergo rapid phase separation, while the open squares denote samples which stay homogeneous. Open diamonds in Fig. 2 represent the results obtained using the second approach. The dotted line in Fig. 2(a) shows a representative tie line which indicates the phase separation process of an initially homogeneous sample [cross in Fig. 2(a)] into two coexisting phases (open diamonds). The phase boundaries in Fig. 2 are a strong function of the size ratio, shifting by more than a factor of 6 in ϕ_s when going from $\xi = 0.09$ to $\xi = 0.29$. It is instructive to compare our experimentally obtained coexistence lines with existing theoretical predictions. Biben and Hansen [3,21] (dot-dashed line in Fig. 2) and Rosenfeld [4,22] (long dashes in Fig. 2) have computed spinodal lines (lines of spontaneous phase separation) of binary fluid hard sphere mixtures. Our expectation that these lines should lie at higher concentrations as compared to the coexistence curves is borne out by our data. While it is difficult to quantitatively compare our data to these theoretical predictions, both show the same trend when ξ is varied. Poon and Warren [23] extend a semianalytical model [24,25] which allows them to compute spinodal lines as well as coexistence curves [19]. While their results for $\xi = 0.14$ are in reasonable agreement with our data ($\xi = 0.13$), a comparison of their theory with our two other data sets is poor; their calculated coexistence curves are essentially ξ independent, while our results show a significant variation with ξ. The observation that phase separation does occur for our largest size ration ($\xi = 0.29$) is of interest, since it is believed [3] that $\xi < 0.25$ is a necessary condition for phase separation to occur. To substantiate this result further and to find the maximum value of ξ^* below which phase separation is observed, we looked for phase separation in samples spanning the range $0.25 \leq \xi \leq 0.35$ for fixed $\phi_\ell = 0.1$ (here, we have also varied the absolute droplet sizes by a factor of 3, with no apparent effect on the phase boundaries [19]). The results of this study are fully consistent with Fig. 2(c) and yield $\xi^* = 0.30 \pm 0.02$. Our experimental data suggest that the lack of phase separation above this value is due to a shift of the phase boundary into a region where the droplet mobility nearly vanishes due to packing constraints. This does not preclude a possible lack of phase separation due to thermodynamic reasons. Note that neutron-scattering studies of a binary colloidal suspension with $\xi = 0.31$ indicate clustering of colloidal spheres, but no macroscopic phase separation [26].

Finally, we address the issue of how well oil droplets can be modeled as hard spheres. While SDS is an ionic surfactant, electrostatic interactions are short ranged due to the screening effect provided by the additional surfactant in the solution (the Debye length is ca. 34 Å). Furthermore, monodisperse emulsions crystallize readily at values of ϕ comparable to those of hard spheres [19]. In emulsions van der Waals forces are weaker than in colloidal dispersions of hard particles, and are further attenuated by the near index-matching conditions. A recent study [17] has addressed the deformability of small oil droplets in emulsions and their surface modes, indicating only a very weak deviation from hard sphere behavior for the oils and sizes used in this study. We are presently conducting dynamic light scattering experiments with a monocomponent emulsion to gain insight into the freezing and melting in this system [19]. Our preliminary results indicate that our emulsions exhibit structural arrest at approximately the volume fraction expected for a hard sphere system [27].

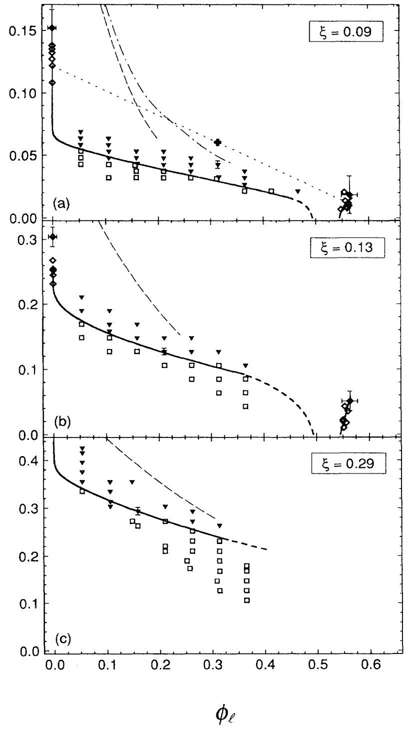

FIG. 2. Phase diagram of three binary mixtures with different size ratios. Solid triangles represent samples which exhibit rapid phase separation, as compared to the open squares where the samples stay homogeneous. Open diamonds indicate the composition of the two phases following phase separation. The solid line is a guide to the eye, representing the experimental coexistence curve, and the short dashes depict an extrapolation motivated by the result of the DLS measurements (see text). The dotted line in (a) indicates a typical tie line, representing the phase separation of a sample in the two phase regions (cross). Long dashes [4] ($\xi = 0.10, 0.17, 0.33$) and the dot-dashed line [21] in (a) ($\xi = 0.10$) indicate spinodal lines obtained by model calculations.

In summary, we have investigated the phase behavior of bidisperse emulsions, covering a large range of relative compositions and size ratios. Nearly index-matched emulsions provide a convenient model system to study mesoscopic hard sphere phenomena, facilitating direct studies using light scattering, microscopy, or visual observation, as compared to colloidal suspensions which are often used in similar experiments. Our results confirm the general phenomenology of phase segregation induced by osmotic depletion forces, as suggested by Biben and Hansen [3]. As pointed out by Rosenfeld [22], quantitative theoretical predictions on the phase behavior of binary hard sphere fluids are difficult to devise, since model calculations depend sensitively on small corrections to the Percus-Yevick equation of state. We hope, therefore, this study will contribute to a better understanding of hard sphere demixing phenomena.

We thank D. Aharoni for her assistance and O. Zik and E. Moses for their help with the interface dynamics measurements, and B. Gorodecki and Y. Hadar for the use of their centrifuge. Fruitful discussions with O. Krichevsky and Y. Rosenfeld are gratefully acknowledged. This research was supported by Grant No. 92-00093/2 from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel. U.S. acknowledges support by the Deutsche Forschungs Gemeinschaft (DFG).

---

[1] J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964).

[2] J. L. Lebowitz, Phys. Rev. **133**, A895 (1964).

[3] T. Biben and J. P. Hansen, Phys. Rev. Lett. **66**, 2215 (1991).

[4] Y. Rosenfeld, Phys. Rev. Lett. **72**, 3831 (1994).

[5] M. Dijkstra and D. Frenkel, Phys. Rev. Lett. **72**, 298 (1994), have studied the related problem of cubes in a cubic lattice.

[6] S. Asakura and F. Oosawa, J. Polym. Sci. **33**, 183 (1958).

[7] A. Vrij, Pure Appl. Chem. **48**, 471 (1976).

[8] Experimental evidence for the osmotic depletion effect between hard spheres and a solid wall is given in P. D. Kaplan, L. P. Faucheux, and A. J. Libchaber, Phys. Rev. Lett. **73**, 2793 (1994).

[9] J. Bibette, D. Roux, and B. Pouligny, J. Phys. II (France) **2**, 401 (1992).

[10] W. C. K. Poon, J. S. Selfe, M. B. Robertson, S. M. Ilett, A. D. Pirie, and P. N. Pusey, J. Phys. II (France) **3**, 1075 (1993).

[11] F. Leal Calderon, J. Bibette, and J. Biais, Europhys. Lett. **23**, 653 (1993).

[12] A. Meller and J. Stavans (to be published).

[13] R. Piazza and G. Di Pietro, Europhys. Lett. **28**, 445 (1994).

[14] S. B. Zimmerman and A. P. Minton, Ann. Rev. Biophys. Biomol. Struct. **22**, 27 (1993).

[15] J. S. van Duijneveldt, A. W. Heinen, and H. N. W. Lekkerkerker, Europhys. Lett. **21**, 369 (1993).

[16] P. D. Kaplan, J. L. Rouke, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **72**, 582 (1994).

[17] H. Gang, A. H. Krall, and D. A. Weitz, Phys. Rev. Lett. **73**, 3435 (1994).

[18] P. Becher, *Emulsions; Theory and Practice* (Reinhold, New York, 1965).

[19] U. Steiner, A. Meller, and J. Stavans (to be published).

[20] A more realistic comparison would exclude the initial rapid segregation, using a subcritical reference sample with $\phi \approx 0.45$. In this case, gravitational effects are truly negligible on the relevant time scale.

[21] T. Biben and J. P. Hansen, J. Phys. Condens. Matter **3**, F65 (1991).

[22] Y. Rosenfeld, J. Phys. Chem. (to be published).

[23] W. C. K. Poon and P. B. Warren, Europhys. Lett. **28**, 513 (1994).

[24] H. N. W. Lekkerkerker, W. C. K. Poon, P. N. Pusey, A. Stroobants, and P. W. Warren, Europhys. Lett. **20**, 559 (1992).

[25] H. N. W. Lekkerkerker and A. Stroobants, Physica **A195**, 387 (1993).

[26] P. Bartlett and R. H. Ottewill, Langmuir **8**, 1919 (1992).

[27] Polydispersity causes this transition to be less sharp compared to more monodisperse colloids: see P. N. Pusey and W. van Megen, Nature (London) **320**, 340 (1986); W. van Megen and S. M. Underwood, Nature (London) **362**, 616 (1993).