

Phase-separation in ion-containing mixtures in electric fields

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When a liquid mixture is subjected to external electric fields, ionic screening leads to field gradients. We point out that, if the mixture is initially in the homogeneous phase, this screening can bring about a robust phase-separation transition with two main features: (i) the phase separation is expected to occur in any electrode geometry, and (ii) the voltage required is typically of the order of 1 V and even less. We discuss several applications of the effect relevant to the field of microfluidics, focusing on the creation of a nanometer-scale lubrication layer in the phase separation process and the modification of the slip length.

The understanding and control of the phase behavior of liquid mixtures is extremely important in everyday life and is becoming equally important in the field of microfluidics (1–4). The behavior of minuscule amounts of liquids has drawn considerable attention lately, both from the aspect of basic research as well as from the relevance to numerous applications using transport of small liquids drops (5), mixing of liquids (6, 7), dielectrophoretic transport of colloidal particles (8), etc.

As one confines himself to ever smaller regions of space, control over the traditional parameters that govern the phase-behavior, such as temperature, pressure, concentration and shear rate, becomes more and more difficult. This control is essential in MicroElectroMechanical Systems, where the ultimate performance of a device is limited by the lubrication of the surrounding liquid (9–14). Electric and magnetic fields, on the contrary, benefit from size reduction because these fields are high near small conducting objects, and therefore are excellent candidates for such a task.

Here, we describe a type of phase transition occurring in ion-containing liquid mixtures under the influence of an external electric field. It has been predicted long ago by Landau and Lifshitz (15) and later by Bedeaux and Mazur (16), Onuki (17) and others, that a spatially uniform electric field can change the critical temperature T_c of mixture by a small amount, typically in the mK range. In liquid mixtures containing dissociated ions, in contrast to the Landau case, the electric field is screened, and the resulting gradients in the field and ion density lead to strong electro- and dielectrophoretic forces that tend to separate the mixture into its components. The phase transition is quite generic, and is virtually independent of the electrode geometry.

The model is presented below, and the resultant formulas for the phase separation are derived. We further discuss the features of the effect and its possible applications.

Model

Consider a binary mixture of two liquids A and B, with dielectric constants ϵ_A and ϵ_B , respectively, containing some amount of dissociated positive and negative ions. When a voltage is applied on a mixture that is initially homogeneous, there are two forces acting on the liquid components. The first one is a dielectrophoretic force: as the ions migrate toward the electrode, the field is screened and, therefore, the high- ϵ liquid is drawn to the electrodes. The second force is electrophoretic in nature: the ions may have a chemical preference to one of the liquids, and,

while drifting to the electrodes, they will “drag” some liquid with them. The two forces can work together or against each other. In general, there is also a process of recombination of positive and negative ions into a neutral complex (18–20), but in this simplified treatment, this process is not allowed. We further restrict our attention to monovalent ions, each of charge $1e$.

We define ϕ as the relative A-liquid composition ($0 < \phi < 1$) and $\rho^\pm$ as the number density of positive/negative ions. We denote u_A^+ and u_B^+ as the interaction energies of a positive ion with the A and B liquids, respectively. The interaction energy between the positive ion and the mixture is therefore

$$u_A^+ \rho^+(\mathbf{r}) \phi(\mathbf{r}) + u_B^+ \rho^+(\mathbf{r}) (1 - \phi(\mathbf{r})) = -\Delta u^+ \rho^+(\mathbf{r}) + \text{const},$$

where $\Delta u^+ \equiv u_B^+ - u_A^+$ measures how much a positive ion prefers to be in a A-liquid environment over a B-liquid one. Similar expression exists for the interaction of the negative ions and the mixture. We can now write the system free-energy as an integral $F = \int f[\phi, \psi] d^3r$, where on the mean-field level the free-energy density f is given by

$$f = f_b(\phi) - \frac{1}{2} \epsilon(\phi) (\nabla \psi)^2 + (\rho^+ - \rho^-) e \psi + k_B T [\rho^+ \ln(v_0 \rho^+) + \rho^- \ln(v_0 \rho^-)] - \lambda^+ \rho^+ - \lambda^- \rho^- - \mu \phi - (\Delta u^+ \rho^+ + \Delta u^- \rho^-) \phi + \text{const}. \quad [1]$$

In the above, $k_B T$ is the thermal energy, ψ is the electrostatic potential obeying the proper boundary conditions, e is the electron charge, v_0 is a molecular volume and $\lambda^\pm$ and μ are the Lagrange multipliers (chemical potentials) of the positive and negative ions and liquid concentration, respectively. The mixture dielectric constant ϵ is assumed to depend on the composition through a quadratic constitutive relation $\epsilon(\phi) = \epsilon_c + \epsilon_1 (\phi - \phi_c) + 1/2 \epsilon_2 (\phi - \phi_c)^2$, where ϕ_c is the critical composition and ϵ_c is $\epsilon(\phi_c)$. Finally, f_b is the bulk energy density of the mixture, which is taken here as a simple Landau expansion in the deviation from the critical composition

$$\frac{v_0}{k_B T} f_b = \frac{1}{2} \frac{T - T_c}{T_c} (\phi - \phi_c)^2 + \frac{d}{24} (\phi - \phi_c)^4, \quad [2]$$

where d is positive. This Landau energy has a transition temperature T_t given by $(T_t - T_c)/T_c = -1/6d(\phi - \phi_c)^2$.

As can be seen from a systematic expansion of the free-energy in small $\phi - \phi_c$ and examination of the quadratic term, at zero ionic preference ($\Delta u = 0$) and nearly uniform electric field E_0 , the transition temperature T_t changes to T^* by the Landau mechanism by an amount $T^* - T_t \approx v_0 \epsilon_2 E_0^2 / k_B$. Similarly, with

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nonzero preference Δu and in the absence of field, T_c changes by an amount $T^* - T_t \approx (\Delta u/k_B T)^2 \rho_0 v_0$, where ρ_0 is the bulk ion number density. Although these shifts to the transition temperature exist, they are negligible compared with the shift that we describe below due to the dielectrophoretic and electrophoretic forces, which manifest mathematically as linear terms in $\phi - \phi_c$ in the free energy.

The free-energy expression Eq. 1 depends on the four fields ψ , $\rho^\pm$, and the deviation from critical composition $\varphi \equiv \phi - \phi_c$; the system equilibrium profile is given by the variational principle with respect to these fields

$$\frac{\delta F}{\delta \varphi} = \frac{k_B T}{v_0} \left[\frac{T - T_c}{T_c} \varphi + \frac{1}{6} d \varphi^3 \right] - \frac{1}{2} (\varepsilon_1 + \varepsilon_2 \varphi) (\nabla \psi)^2 - \Delta u^+ \rho^+ - \Delta u^- \rho^- - \mu = 0 \quad [3]$$

$$\frac{\delta F}{\delta \psi} = \nabla \left[\left(\varepsilon_c + \varepsilon_1 \varphi + \frac{1}{2} \varepsilon_2 \varphi^2 \right) \nabla \psi \right] + e(\rho^+ - \rho^-) = 0 \quad [4]$$

$$\frac{\delta F}{\delta \rho^\pm} = \pm e \varphi + k_B T (\ln \rho^\pm + 1) - \Delta u^\pm \varphi - \lambda^\pm = 0. \quad [5]$$

The second equation above is the Poisson equation. For concreteness, we consider two simple one-dimensional cases where the mixture is bounded by either two walls at $x = 0$ and $x = L$ with potentials $\psi(0) = V$ and $\psi(L) = -V$, or bounded to the half space $x \geq 0$ by a single wall at $x = 0$ with potentials $\psi(0) = V$ and $\psi(\infty) = 0$. For simplicity, we assume $\Delta u^+ = \Delta u^- = \Delta u$, and that far enough from the walls where the potential is zero, the system is coupled to a reservoir at mixture composition ϕ_0 and ion concentration ρ_0 .

Inadequacy of the Linear Poisson–Boltzmann Approximation. In field-induced phase-separation, the required fields should be of the order $E \gtrsim 10^6$ V/ μm (21). The linearized Poisson–Boltzmann equation for a homogeneous mixture with uniform dielectric constant ε gives the field E near one wall at $x = 0$ with potential V to be exponentially decaying: $E = \lambda_D^{-1} V e^{-x/\lambda_D}$, where λ_D is the Debye screening length given by $\lambda_D^{-2} = 2\rho_0 e^2 / (\varepsilon k_B T)$. For typical values of λ_D the field $E \propto V$ is thus too small because the potential is small, $eV \ll k_B T$.

Phase Separation. As pointed above, the creation of high- and low-field regions due to ionic screening leads to a dielectrophoretic force which tends to “suck” the high- ε material (assumed to be A) toward the region with high field. If fields gradients are small, the mixtures composition changes smoothly in the vicinity of the electrodes. However, if the field gradients are large enough, the A-liquid composition crosses into the unstable part of the phase-diagram, and a discontinuous composition profile ϕ occurs, signifying a phase-transition (21). As a first approximation, we can use the well known analytical expressions for the potential and ion distributions for a medium with uniform dielectric constant $\varepsilon = \varepsilon_c$, and these can be substituted in Eq. 3. Such an approximation is justified because field gradients are mainly due to the ions and are much less influenced by the mixture composition. As a result, analysis along classical lines (22) predicts that the transition temperature changes from T_t to T^* under the influence of an external field, such that

$$\frac{T^* - T_t}{T_c} \approx \left(\frac{|\varepsilon_1|}{\varepsilon_c} + \frac{\Delta u}{k_B T_c} \right) \frac{\rho_0 v_0}{|\phi_0 - \phi_c|} \exp \left(\frac{eV}{k_B T_c} \right). \quad [6]$$

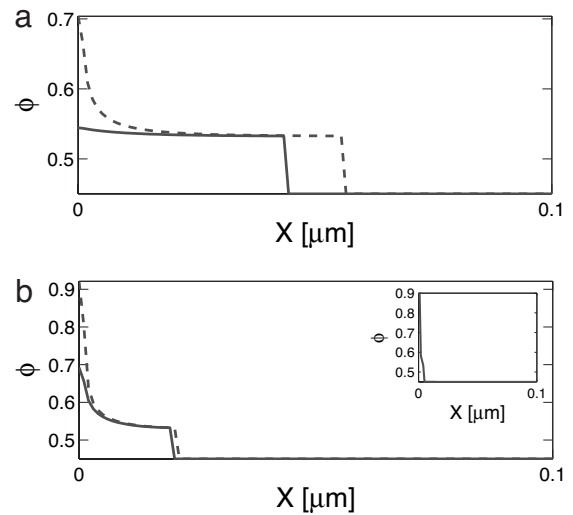


Fig. 1. Composition profiles $\phi(x)$ for a mixture in the vicinity of one wall at potential V at $x = 0$. Solid lines correspond to $V = 0.2$ V and dashed lines to $V = 0.4$ V. Far from the wall, the bulk composition is $\phi = 0.45$ and the bulk ion concentration corresponds to pH 7 (a) and pH 10 (b). (Inset) $V = 0.4$ V and pH 12. In all plots, the temperature is 1 K above the transition temperature, the molecular volume is $v_0 = 8 \times 10^{-27}$ m³ and the dielectric constants are $\varepsilon_A = 3$ and $\varepsilon_B = 2$.

This expression holds as long as T^* is smaller than T_c ; at all temperatures $T > T_c$, the composition profile $\phi(x)$ varies smoothly with no abrupt jump.

It is now clear that the dielectrophoretic force, proportional to the dielectric mismatch ε_1 , and the electrophoretic force, proportional to Δu , should be treated on equal footing. Note that, for many liquid pairs, $|\varepsilon_1|/\varepsilon_c \approx 1$ and $\Delta u/k_B T \approx 1$, and that $\rho_0 v_0$ is small: for a liquid with molecular volume $v_0 = 8 \times 10^{-27}$ m³ and ion content of pure water we have $\rho_0 v_0 \approx 5 \times 10^{-7}$. In addition, the denominator has a factor that measures the distance from the critical composition, similar to the expression for demixing in ion-free solutions. However, the most striking feature of Eq. 6 is the exponential factor, which can be huge: already at only 0.5 V and at room temperature $\exp(eV/k_B T) \approx 4.8 \times 10^8$. Different voltages change these figures dramatically, but clearly the shift of the transition temperature can be very large. Although the parameters determining the Debye length all appear in Eq. 6, λ_D does not appear explicitly due to the nonlinearity of the current theory.

Fig. 1a shows the composition profile $\phi(x)$ calculated numerically from Eqs. 3, 4, and 5 for one wall at $x = 0$ with potential $\psi(x = 0) = V$, for two different potentials above the threshold for demixing: $V = 0.2$ V (solid line) and $V = 0.4$ V (dashed line). The ionic content is the same as in a pH 7 solution (e.g., pure water). A clear front is seen separating A-rich (large ϕ) and A-poor (small ϕ) domains. The A-liquid enrichment at the wall is larger with the higher voltage. Fig. 1b is the same, but the ion density is much larger, corresponding to pH 10. The phase separation front is created closer to the wall. Inset shows the profile when $V = 0.4$ V and the pH is 12.

Discussion

From Eq. 6, we see that a liquid mixture phase-separates into its components when put under the influence of an electric field in some reasonable conditions. The dissociated ions in the solution are important because they bring about large field gradients even in a flat electrode geometry. Field gradients give rise to a dielectrophoretic force that acts to pull the liquid with high dielectric constant toward the region with high field (low di-

electric component is attracted to the low field). This tendency is accompanied by another equally important electrophoretic tendency, where the ions attracted to the electrodes preferentially “drag” with them one of the liquid components. This second effect can enhance or negate the dielectrophoretic phase separation, depending on the solubility of the ions in the liquid components.

For small enough potential, the composition of the A liquid component (high dielectric constant) is enhanced close to the walls, but the profile remains smooth. There exists a threshold voltage V_c above which phase-separation occurs, and the composition profile changes dramatically: A-rich and A-poor domains are separated by a sharp interface (21). The thickness of the A-rich domain can be extremely small, and depends nonlinearly on the ionic content in solution as well as on the applied voltage.

For an ion-containing mixture, the nonlinear dependency on the voltage means that increase in V changes the field's spatial distribution in addition to its amplitude. This is in contrast to ion-free mixtures, where the applied voltage does not affect the field distribution, only the amplitude (21). As a result, in ionic mixtures increase of the voltage increases the composition difference between phase-separated domains and may increase or decreases the thickness of the enrichment layer close to the electrodes. Thus, the physics of the phase separation considered here is unique.

The field-induced phase separation has some important implications in several circumstances. The first one relates to the rheological behavior in systems with moving parts, that is field-controlled lubrication. This is reminiscent of pressure-induced melting in ice skating, but apparently richer. Consider two sub-micrometer-scale objects sliding past another so that the mixture confined between them is sheared under conditions of low Reynold numbers (11, 23–26). Let us denote the viscosities of the A and B liquids by η_A and η_B , respectively. In the absence of field (mixed state) and under constant applied external stress, the mixture will have the homogeneous viscosity η_m , and the two surfaces will slide with a certain velocity v_m with respect to each other. In the presence of electric field (demixed state), the fluid exhibits layers of different viscosities parallel to the walls (9–11). When the same stress is applied across these layers, the surfaces move at a relative velocity v_d . If the components' viscosities are very different, $\eta_B \gg \eta_A$, the velocity gradient falls on a very thin layer of the less viscous liquid, and it then follows that v_d is much larger than v_m , $v_d/v_m \approx \eta_B/\eta_A$. Essentially, the phase-separated mixture has a smaller effective viscosity than the homogeneous one. This state is reversible: when the field is turned off, the mixture becomes homogeneous again. In a typical binary mixture of alkanes and siloxane oils (squalane and polymethylphenylsiloxane), the viscosity ratio is ≈ 10 ; thus, the effective viscosity of the demixed liquid is decreased by a factor 10 as compared with

the mixed solution. A different prominent example is a water-glycerol mixture, where the velocity ratio is expected to be $v_d/v_m \approx 1,500$. However, note that we do not expect a real phase-transition here but rather simply the creation of enrichment layers at the surfaces. Other liquid pairs may prove to be more useful. We also point out that the creation of viscosity layers at the surface is equivalent to changing the slip length. Thus, in pressure-driven flows and depending on the geometry one may be able to change, say, Poiseuille flow into plug flow, or vice versa, at a given moment and location.

Phase-separation could also be interesting in chemical reactions: when two or more chemical species are undergoing a chemical reaction in a liquid environment, application of an electric field can be used to phase-separate the liquids. This phase separation can have two consequences: (i) If the reactant species exist preferentially in one liquid component (say A), phase separation will lead to their accumulation into the A-rich environment, and to acceleration of reaction kinetics in a highly confined region of space ($\approx 1 \mu\text{m}$). (ii) If the reactant species prefer different liquid components, after field-induced phase separation, the reaction will be limited to the interface between coexisting phases and consequently slowed down. The phase-transition has some consequences in microfluidics optics (4), because, in general, the liquid components have different index of refraction. A light wave will not be deflected if it were to pass in a homogeneous mixture and if the components are transparent enough. However, once demixing occurs, interfaces between coexisting phases will scatter, deflect, or refract the light, and this could be used to create optical switches or lenses in a microfluidic system coupled to an external light source (ref. 4 and unpublished data). Here again, the reversibility of the phase separation is a boon. Lastly, we mention that the electric field drops off rapidly in the vicinity of highly charged objects in solutions, and that the resulting field gradients could lead to local phase-separation around charged colloids. For a colloid of size $R = 1 \mu\text{m}$ in ion-free solution of dielectric constant $\epsilon = 10\epsilon_0$, the field near the colloid's surface is $E = Q/(\epsilon R^2)$, and the charge Q for separation is of the order of $1,000 e$. In salty solution with $\lambda_D \approx 50 \text{ nm}$, the field is $E \approx V/\lambda_D$ and phase-separation is expected to occur when the colloid potential is $V \approx 0.1 \text{ V}$.

This peculiar phase separation could be further explored in the directions outlined above. The dependence of demixing on the frequency of applied external field and the dynamics of field-induced phase separation should be studied as well.

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