

Stabilization of charged and neutral colloids in salty mixtures

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We present a mechanism for the stabilization of colloids in liquid mixtures without use of surfactants or polymers. When a suitable salt is added to a solvent mixture, the coupling of the colloid's surface chemistry and the preferential solvation of ions leads to a repulsive force between colloids that can overcome van der Waals attraction. This repulsive force is substantial in a large range of temperatures, mixture composition, and salt concentrations. The increased repulsion due to addition of salt occurs even for charged colloids. This mechanism may be useful in experimental situations where steric stabilization with surfactants or polymers is undesired. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4851477>]

The stability of colloidal dispersions is essential in material science and technology. Steric stabilization of colloids against the attractive van der Waals (vdW) forces can be achieved using surfactant or polymer molecules that are physically or chemically attached to the colloid's surface. Charged colloids can also be stabilized via the screened Coulomb repulsion, whose range depends on the Debye length κ^{-1} . In the celebrated Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory, addition of salt to the suspension decreases the Debye length and the electrostatic repulsion leading eventually to coagulation and sedimentation of the colloids.¹

In recent years, we began to better understand the differences between the electrostatics of pure solvents compared to liquid mixtures. The preferential wetting of one liquid component at the colloid surface^{2,3} affects the density of the ions, the electrostatics of the mixture, and the interaction between the colloids.⁴⁻¹² A key parameter is the selective solvation of the ions in the liquids.¹³⁻²²

In this paper, we present a new method for the stabilization of electrically charged or neutral particles in solvent mixtures by *addition* of salt, without use of surfactants or polymers. The stabilization relies on (i) selective adsorption of one solvent on the colloids and (ii) a difference in the preferential solubilities of the anion and the cation in the solvents, namely, a difference between the Gibbs transfer energy of moving the anion from one solvent to the other and the analogous Gibbs energy of the cation. These energies are often larger than the thermal energy^{23,24} and therefore particles can be stabilized even without other additives. In fact, requirements (i) and (ii) above are generally met because any surface is hydrophilic or hydrophobic to some extent and no two ions have identical solvation energies.^{23,24} The coupling of the colloid's surface chemistry and the preferential solvation of ions leads to a repulsive force between colloids that can overcome the van der Waals attraction. This repulsive force is large in an unexpectedly wide range of temperatures, mixture compositions, and salt concentrations. This method preserves the chemical properties of the surface and therefore is advantageous in cases

where surfactants, polymers, or a chemical modification of the particle are undesired.

We consider relatively dilute mixtures in which ion-ion correlations effects are small.^{25,26} In order to isolate the effect of preferential solvation, we ignore specific ion-surface interactions.^{27,28} These short range interactions can either enhance or counteract the stabilization mechanism we discuss and their magnitude is of specific nature.

We focus on a system composed of a binary aqueous mixture containing a 1:1 monovalent salt and confined between two identical flat plates. The plates are located at $z = \pm D/2$ and their area is S . The mixture composition is given by the water volume fraction ϕ ($0 \leq \phi \leq 1$) while the cosolvent composition is given by $1 - \phi$. The number densities of the point-like positive and negative ions are denoted by n^\pm . The fluid between the plates is in contact with an electroneutral matter reservoir at composition ϕ_0 and a salt concentration n_0 .

The mean-field free energy density of the system is given by¹⁷

$$f = k_B T \left[f_m(\phi) + \frac{1}{2} C |\nabla \phi|^2 \right] - \frac{1}{2} \varepsilon_0 \varepsilon(\phi) (\nabla \psi)^2 + e(n^+ - n^-) \psi + k_B T \sum_{i=\pm} n^i [(\log(v_0 n^i) - 1) - \Delta u^i \phi], \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature, ε_0 is the vacuum permittivity, and $v_0 = a^3$ is the molecular volume. $v_0 f_m$ is the dimensionless mixing free energy density: $v_0 f_m = \phi \log(\phi) + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi)$, where the Flory parameter is $\chi \sim 1/T$. The mixture demixes for $T < T_c$ ($\chi > \chi_c = 2$). The energetic cost of composition inhomogeneities is accounted for by the square-gradient term, where C is a positive constant with units of inverse length. In the electrostatic energy in Eq. (1), ψ is the electric potential and ε is the dielectric constant, assumed to depend linearly on composition by $\varepsilon(\phi) = \varepsilon_c + (\varepsilon_w - \varepsilon_c)\phi$, where ε_w and ε_c are the water and cosolvent dielectric constants, respectively. The first term on the second line of Eq. (1) is the ions' electrostatic energy, where e is the elementary charge. The first term in

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the sum is the ideal-gas entropy of the ions and the second term is the ion solvation energy. In our simple theory, the solvation energy is proportional to the local solvent composition and its strength is measured by the parameters Δu^i .^{13,14} Here, we are interested in salts where the asymmetry in the cation and anion solvation parameters, defined as $\nu \equiv (\Delta u^+ - \Delta u^-)/2$, is large. This is commonly satisfied in antagonistic salts where one ion is hydrophilic and the other is hydrophobic: $\Delta u^+ \Delta u^- < 0$.

The short range and electrostatic interactions between the fluid and the solid surfaces are given by the surface free energy density f_s

$$f_s = k_B T \Delta \gamma \phi(\mathbf{r}_s) + e\sigma \psi(\mathbf{r}_s), \quad (2)$$

where \mathbf{r}_s is a vector on the colloid surface and $e\sigma$ is the surface charge density of the plates. The surface wettability is given by the parameter $\Delta \gamma$ that measures the difference between the solid-water and solid-cosolvent surface tensions.

The equilibrium state of the system is found by extremization of the grand potential

$$\Omega = \int [f - k_B T (\lambda_0^+ n^+ + \lambda_0^- n^- + \mu_0 \phi)] d\mathbf{r} + \int f_s d\mathbf{r}_s,$$

where λ_0^\pm and μ_0 are the chemical potentials imposed by the species in the reservoir. This leads to the first Euler-Lagrange (EL) equation $\delta \Omega / \delta \phi = 0$

$$-C \nabla^2 \phi + \frac{\partial f_m}{\partial \phi} - \sum_{i=\pm} \Delta u^i n^i - \varepsilon_0 \frac{d\varepsilon/d\phi}{2k_B T} (\nabla \psi)^2 = \mu_0, \quad (3)$$

with the boundary condition $\mathbf{n} \cdot \nabla \phi = \Delta \gamma / C$, where \mathbf{n} is a unit vector perpendicular to the surface. The EL equation for the potential $\delta \Omega / \delta \psi = 0$ naturally yields Gauss' law: $-\nabla \cdot (\varepsilon_0 \varepsilon(\phi) \nabla \psi) = e(n^+ - n^-)$ with the boundary condition $-\mathbf{n} \cdot \nabla \psi = e\sigma / \varepsilon_0 \varepsilon(\phi)$. The densities n^\pm from $\delta \Omega / \delta n^\pm = 0$ obey the Boltzmann distribution $n^\pm = v_0^{-1} \exp(\mp \Psi + \Delta u^\pm \phi + \lambda_0^\pm)$, where $\Psi = e\psi / k_B T$ is the dimensionless potential.

A solution of the EL equations in a planar geometry yields the one-dimensional profiles $\phi(z)$, $\psi(z)$, and $n^\pm(z)$. In Fig. 1, we plot the resulting profiles for a salty mixture between two electrically neutral and hydrophobic plates with a wettability $\Delta \gamma = 0.2/a^2$. The mixture has a bulk critical composition, $\phi_0 = 1/2$, and its temperature is far above T_c , $\Delta T = T - T_c = 21.5$ K. The bulk concentration of the antagonistic salt is $n_0 = 20$ mM and the solvation parameters are $\Delta u^+ = -\Delta u^- = \nu = 6$.

The ionic profiles in Fig. 1(b) show that an electrostatic diffuse layer (EDL) is realized near the plates, despite their electric neutrality. The reason is the adsorption of the cosolvent on the hydrophobic plates shown by the profile of ϕ in Fig. 1(a). The cosolvent ‘‘drags’’ the hydrophobic anions and repels the hydrophilic cations. Hence, a net charge density develops in the vicinity of the plates, giving rise to the electric potential profile shown in Fig. 1(a).

The width of the adsorbed fluid layer is comparable to the bulk correlation length ξ . Beyond this distance $\phi(z)$ decays to its bulk value. However, electroneutrality dictates that the ionic profiles must compensate for the deviation from the bulk values near the plate. At surface separation of

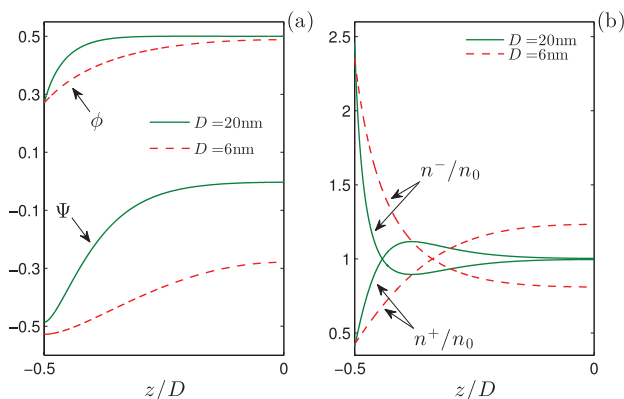


FIG. 1. Profiles of the (a) composition, dimensionless potential, and (b) scaled ion densities between two electrically neutral plates immersed in a critical mixture ($\phi_0 = 1/2$) at a temperature $\Delta T = T - T_c = 21.5$ K and containing 20 mM of antagonistic salt ($\Delta u^+ = -\Delta u^- = \nu = 6$). Here and in other figures, the plates are hydrophobic with $\Delta \gamma = 0.2/a^2$, corresponding to about 7 mN/m. As an approximation to water–2,6-lutidine mixtures, we used $T_c = 307.2$ K, $v_0 = 39 \text{ \AA}^3$, $C = \chi/a$,²⁹ $\varepsilon_{\text{lutidine}} = 6.9$, and $\varepsilon_{\text{water}} = 79.5$.

$D = 20$ nm (Fig. 1(b), solid curves), this means that the anion (cation) concentration becomes smaller (larger) than the bulk value n_0 before it decays to n_0 at the midplane ($z = 0$), leading to a minimum (maximum) in the profile. On the other hand, at a distance of $D = 6$ nm, the extremum is missing since the EDLs from each plate overlap, such that $n^\pm(z = 0) \neq n_0$. Such an overlap implies a repulsive osmotic force between the plates.

Using the profiles we calculate the osmotic pressure Π between the plates at a given distance D from $\Pi(D) = P_{zz} - P_0$, where $P_{zz} = \phi \delta f / \delta \phi + n^+ \delta f / \delta n^+ + n^- \delta f / \delta n^- - f - \varepsilon_0 \varepsilon(\phi) (\partial \psi / \partial z)^2$ is the zz component of the Maxwell pressure tensor¹⁷ and $P_0 = P_{zz}(\phi_0, n_0^\pm, \psi = 0)$ is the bulk pressure. The interaction potential $U(D)$ between the plates is obtained from the osmotic pressure via $U(D) = -S \int_\infty^D \Pi(D') dD'$.

The interaction potential for the parameters of Fig. 1 with solvation asymmetry $\nu = 6$ is plotted in Fig. 2 (red curve). At close separations the potential is attractive due to adsorption of the cosolvent on the plates, but a repulsive barrier of $\approx 10k_B T$ appears in $U(D)$ at a distance denoted by D_{max} of a few nanometers. The barrier height $U_{\text{max}} = U(D_{\text{max}})$ strongly depends on ν . For an antagonistic salt with $\nu = 4$ (blue curve), the barrier is much smaller, while for a hydrophilic salt with $\nu = 0$ (green curve), the potential is purely attractive.

In order to better understand the physical origin of the repulsion, we examine the components of the osmotic pressure. For symmetric plates, Π can be recast in term of the mid-plane composition $\phi_m = \phi(z = 0; D)$ and ion densities $n_m^\pm = n^\pm(z = 0; D)$ as $\Pi(D) = \Pi_{\text{ions}}(n_m^\pm) - \Pi_{\text{mix}}(\phi_m)$, where

$$\Pi_{\text{ions}} = k_B T (n_m^+ + n_m^- - 2n_0), \quad (4)$$

$$\Pi_{\text{mix}} = k_B T (f_m(\phi_m) - f_m(\phi_0) - \mu_0(\phi_m - \phi_0)). \quad (5)$$

The inset of Fig. 2 shows Π_{ions} and Π_{mix} for the $\nu = 6$ potential curve. It is seen that Π_{ions} is repulsive at $D \gtrsim 4$ nm; when the EDLs overlap this leads to an increase of n_m^\pm . $-\Pi_{\text{mix}}$ on the other hand is attractive. Since U is the cumulative

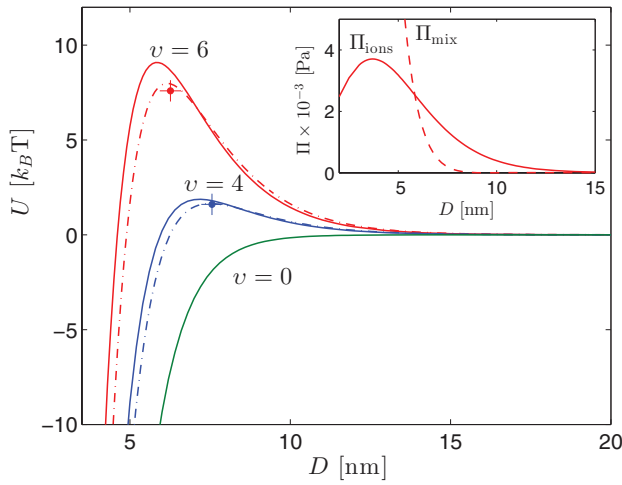


FIG. 2. The interaction potential $U(D)$ between electrically neutral and hydrophobic plates immersed in a mixture with ϕ_0 , T , and n_0 as in Fig. 1. When both ions are hydrophilic the interaction is purely attractive ($\Delta u^\pm = 6$, green curve). A weak repulsive barrier U_{\max} appears with antagonistic salts ($\Delta u^+ = -\Delta u^- = 4$, blue curve), and its height increases with increasing $\Delta u^+ - \Delta u^-$ ($\Delta u^+ = -\Delta u^- = 6$, red curve). Full numerical solutions (solid curves) are in good agreement with linear theory (dashed-dotted curves), where we used $\kappa^{-1} = 1.68$ nm, $\xi = 0.94$ nm, and $l = 1.78$. Two crosses are the approximation (D_{\max} , U_{\max}) of Eq. (14). Inset: The two components of the osmotic pressure (see text) for the red curve. Here and in Fig. 3, the area of the hydrophobic plates is $S = 0.01 \mu\text{m}^2$ and $\Delta\gamma = 0.2a^2$.

integral of $\Pi_{\text{ions}} - \Pi_{\text{mix}}$, a repulsive barrier is created by a range of D for which $\Pi_{\text{ions}} > \Pi_{\text{mix}}$, corresponding to $D \gtrsim 6$ nm in the figure.

To better characterize the repulsive potential, we solve the governing equations in the limit where the perturbations in the composition $\varphi = \phi - \phi_0$ and ion densities $\delta n^\pm = n^\pm - n_0$ are small:¹⁸ $\delta n^\pm = n_0(\Delta u^\pm \varphi \mp \Psi)$, $\kappa^{-2} \nabla^2 \Psi = \Psi - \nu \varphi$, $\kappa^{-2} \nabla^2 \varphi = l^2 \varphi + \omega^2(\Psi/\nu - \varphi)$, where $\kappa = (2l_B n_0)^{1/2}$ is the Debye wavenumber and $\omega = |\nu|/(l_B C)^{1/2}$ is a scaled ν . Here, $l_B = e^2/(\epsilon_0 \epsilon(\phi_0) k_B T)$ is the Bjerrum length at ϕ_0 and $l = 1/\kappa \xi$ is the ratio of the Debye length and the modified correlation length ξ : $\xi = (C/\tau)^{1/2}$, where $\tau = \partial^2 f_m(\phi_0)/\partial \phi^2 - n_0(\Delta u^+ + \Delta u^-)^2/2$.

The solution of the linear equations with the $z \rightarrow -z$ symmetry is

$$\Psi(z) = a_1 \cosh(q_1 z) - a_2 \cosh(q_2 z), \quad (6)$$

$$\varphi(z) = b_1 \cosh(q_1 z) - b_2 \cosh(q_2 z). \quad (7)$$

The wavenumbers q_i obey

$$(q_i/\kappa)^4 - (1 + l^2 - \omega^2)(q_i/\kappa)^2 + l^2 = 0. \quad (8)$$

The amplitudes a_i and b_i are determined using the boundary conditions; in the special case where the plates are electrically neutral they are

$$a_i = \frac{\Delta\gamma}{C} \frac{\kappa^2 \nu}{q_i(q_2^2 - q_1^2) \sinh(q_i D/2)}, \quad (9)$$

$$b_i = \frac{\Delta\gamma}{C} \frac{q_i^2 - \kappa^2}{q_i(q_2^2 - q_1^2) \sinh(q_i D/2)}. \quad (10)$$

In the linear case, it follows that

$$\frac{U}{k_B T} = S \times \frac{(\Delta\gamma)^2}{2C} \left[\Lambda_1 \frac{\coth(q_1 D/2) - 1}{q_1} - \Lambda_2 \frac{\coth(q_2 D/2) - 1}{q_2} \right], \quad (11)$$

where

$$\Lambda_i = \frac{q_i^2 - \kappa^2}{q_2^2 - q_1^2}. \quad (12)$$

One can see from Eq. (11) that the interaction is $\propto (\Delta\gamma)^2$ and that the interplay between the two terms in brackets determines the nature of U . In the limit of vanishing solvation asymmetry $\omega \rightarrow 0$, we have from Eq. (8): $q_1 \rightarrow \kappa$ and $q_2 \rightarrow \xi^{-1}$, leading to $\Lambda_1 \rightarrow 0$ and $\Lambda_2 \rightarrow 1$. The resulting potential is attractive, as expected when ion solvation is absent due to critical adsorption.³⁰

For non-vanishing ω , we focus on the region above T_c for which $l > 1 + \omega$ and hence both q_1 and q_2 are positive real numbers. For sufficiently small ω , we find

$$q_1 \cong \kappa \sqrt{1 + \frac{\omega^2}{l^2 - 1}}, \quad q_2 \cong \xi^{-1} \sqrt{1 - \frac{\omega^2}{l^2 - 1}}. \quad (13)$$

In this region, it is easy to show that $q_2 > q_1 > \kappa$ and thus $\Lambda_1 > 0$ and $\Lambda_2 > 0$. Therefore, the first term in brackets in Eq. (11) is repulsive while the second is attractive, leading to the existence of a maximum in the potential. The location and magnitude of this repulsive barrier are found by solving $\partial U/\partial D = 0$. In the limit $D \gg q_1^{-1}, q_2^{-1}$, we find for D_{\max} and U_{\max}

$$D_{\max} = \frac{\log(\Lambda_2/\Lambda_1)}{q_2 - q_1}, \quad (14)$$

$$\frac{U_{\max}}{k_B T} = S \times \frac{(\Delta\gamma)^2}{C} \left[\frac{\Lambda_1}{q_1} \left(\frac{\Lambda_2}{\Lambda_1} \right)^{\frac{q_1}{q_2 - q_1}} - \frac{\Lambda_2}{q_2} \left(\frac{\Lambda_2}{\Lambda_1} \right)^{\frac{q_2}{q_2 - q_1}} \right].$$

Whether U_{\max} is significant depends on the ratio of amplitudes Λ_2/Λ_1 .

At large enough colloid separations D , the repulsive tail of the interaction is $U/k_B T \simeq S(\Delta\gamma)^2/(C/\Lambda_1) \exp(-q_1 D)/q_1$. This expression is analogous to the regular Debye-Hückel result $U/k_B T \simeq S(\sigma^2/\epsilon_0 \epsilon) \exp(-\kappa D)/\kappa$ for charged colloids.¹ In our theory, q_1 is a modified Debye wavenumber, C/Λ_1 is a property of the medium, and $\Delta\gamma$ plays the role of an effective surface charge, reflecting the properties of the surface.

The comparison between the full potential and the analytical approximation Eq. (11) is shown in Fig. 2. For both $\nu = 6$ ($\omega = 0.64$) and $\nu = 4$ ($\omega = 0.43$), the linear theory (dashed-dotted curves) agrees quite well with the numerical solution (solid curves). Two circles in Fig. 2 show D_{\max} and U_{\max} evaluated using Eq. (14). Our analysis shows that q_1 and Λ_1 must be large enough for significant repulsion to appear. Hence, from Eq. (13) and Eq. (12) we conclude that ω should not be too small and l not too large. The first requirement is satisfied by choosing antagonistic salts while the second dictates the temperature window given the salt concentration.

The two experimentally important quantities U_{\max} and D_{\max} are plotted in Figs. 3(a) and 3(b), respectively. For

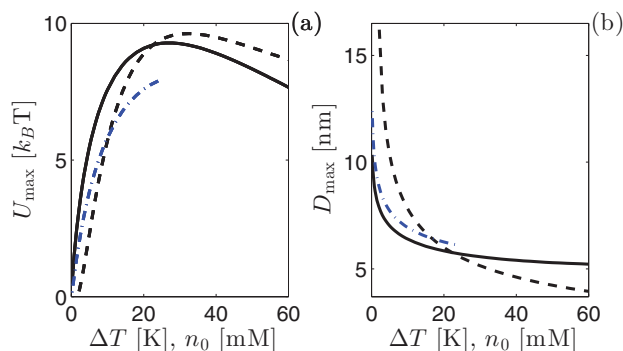


FIG. 3. (a) Barrier height and (b) location as a function of ΔT and n_0 for $\nu = 6$ and $\Delta\gamma = 0.2/a^2$. Dashed curves are numerical results for $\phi_0 = 0.5$, $n_0 = 20$ mM, and varying ΔT ; a repulsive barrier appears at $\Delta T \gtrsim 2$ K. For the solid curves, $\phi_0 = 0.5$, $\Delta T = 21.5$ K, and n_0 varies. Dashed-dotted curves are Eq. (14) for varying n_0 plotted in the validity range given by $l > 1 + \omega$.

increasing ΔT (dashed curves), a repulsive barrier first appears at $\Delta T \approx 2$ K, and it has a maximal value. The solid curves give results for varying n_0 , showing again a maximum in U_{\max} . Dashed-dotted lines are U_{\max} and D_{\max} vs n_0 from Eq. (14) in the range $l > 1 + \omega$. Fig. 3(a) shows that stabilization can be achieved far above the critical temperature. Thus, in principle the theory applies to experiments with completely miscible mixtures, e.g., water and alcohol, which in our theory is the $\chi \rightarrow 0$ limit of athermal mixtures.

The behavior of U_{\max} is determined by the interplay between the attractive adsorption-related part of interaction and the repulsive solvation-related part. An increase in ΔT or n_0 increases ξ^{-1} or κ , respectively. The result in both cases is an increase in the wavenumbers q_i and therefore a decrease in D_{\max} , see Fig. 3(b). Furthermore, the relative magnitudes of the wavenumbers q_i and the amplitudes Λ_i change in a non-trivial manner due to the coupling of the attractive and repulsive contributions, given by the parameter l in the linear theory.

In the spirit of the DLVO theory, the more realistic case of spherical colloids of radius R is evaluated by applying Derjaguin's approximation to the potential U and adding the vdW interaction between the spheres: $U_T = \pi R \int_D^\infty U(D')dD' - A_H R/(12D)$, where A_H is the Hamaker constant. Contours of the maximum of U_T , $U_{T,\max}$, are shown in Fig. 4(a) in the ϕ_0 - T plane. Notice that $U_{T,\max}$ increases significantly for water-rich compositions ($\phi_0 > 0.5$). The reason for this is twofold: (i) the adsorption force is weaker at off-critical compositions and (ii) relative to the bulk composition, the water-poor layer on the surface is more attractive for hydrophobic ions. For hydrophilic colloids ($\Delta\gamma < 0$), $U_{T,\max}$ would be larger at compositions $\phi_0 < 0.5$. While the absolute values of $U_{T,\max}$ do not depend on the sign of $\Delta\gamma$, the hydrophobicity or hydrophilicity of the colloids determines the ideal working region in the ϕ_0 - T plane. The contour lines of $U_{T,\max} = 3k_B T$ are shown in Fig. 4(b) for different values of the Hamaker constant. The area enclosed by this contour defines approximately the working conditions for a stable dispersion. Indeed, even for large values of the Hamaker constant a stable region exists for water-rich compositions and closer to the binodal curve. Hence, one could add only a small amount of

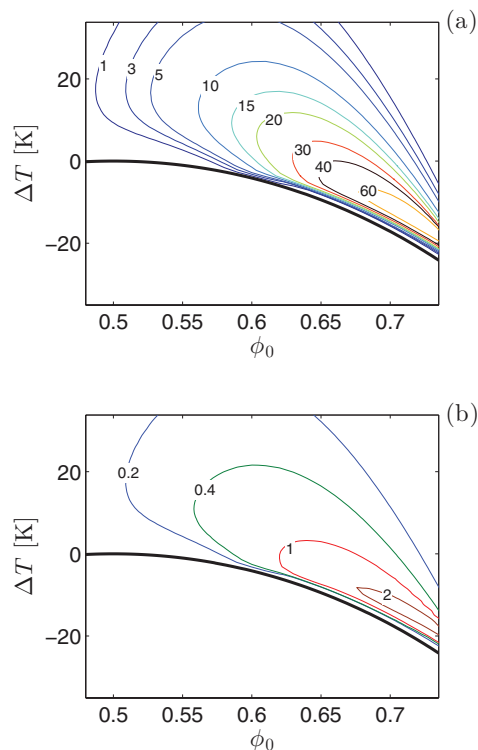


FIG. 4. The maximum of the interaction potential, $U_{T,\max}(\phi_0, T)$, in the ϕ_0 - T plane including vdW attraction and using Derjaguin's approximation for a colloid radius $R = 1 \mu\text{m}$. (a) Contours of $U_{T,\max}$ for a Hamaker constant $A_H = 0.2 \times 10^{-20}$ J. (b) The contour lines corresponding to $U_{T,\max} = 3k_B T$ for different Hamaker constants. The values of Hamaker's constant are indicated by the labels in units of 10^{-20} J. Here, $\nu = 6$, $n_0 = 20$ mM, and $\Delta\gamma = 0.2/a^2$.

co-solvent to an unstable dispersion of charge-free colloids to obtain a stable dispersion.

The linear solvation model adopted by us for its simplicity is a first-order approximation, and the study of more complex and realistic solvation models is an active area of research.²² Nonetheless, the large repulsive barriers we predict are not restricted to a linear solvation model.³¹ In addition, a significant barrier can also be obtained for weakly antagonistic salts ($\nu \simeq 1$) if the plates are made more hydrophobic or hydrophilic (Eq. (11)), or if the bulk composition is changed (Fig. 4(a)).

In Fig. 5, we show that addition of antagonistic salts can enhance the stability of *charged* colloids as well. When the colloids' surface and the ions are indifferent to the solvents, $\Delta\gamma = 0$ and $\Delta u^\pm = 0$, as in the regular Poisson-Boltzmann theory, the effect of the mixture on the interaction is via the dependence of the dielectric constant on ϕ . The result for $U_T(D)$, shown by the solid curve in Fig. 5, is a marginally stable potential. For hydrophobic colloids ($\Delta\gamma > 0$), U_T becomes attractive if the salt is hydrophilic (dashed curve), indicating a destabilization of the suspension. However, for hydrophobic colloids and an antagonistic salt (dashed-dotted curve) the repulsive barrier increases significantly, indicating a stabilization of the suspension. Here, the hydrophobic and positively charged colloids draw a larger amount of hydrophobic anions towards their surface, leading to an increase in the repulsive osmotic pressure of ions.

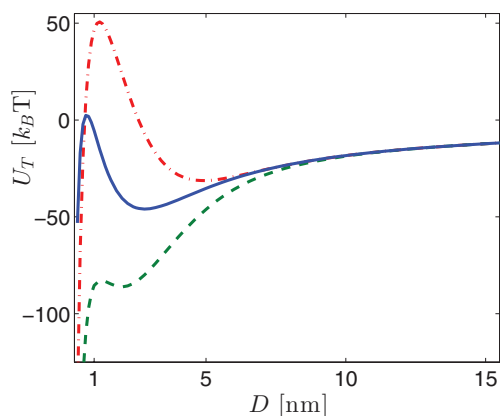


FIG. 5. $U_T(D)$ for two charged colloids with a surface charge density $\sigma = 0.1 \text{ nm}^{-2}$. When $\Delta\gamma = 0$ and $\Delta u^\pm = 0$ (solid curve), the potential is marginally stable. For a hydrophobic surface, $\Delta\gamma = 0.2/a^2$, the potential is unstable for a hydrophilic salt ($\Delta u^\pm = 6$, dashed curve) while it has a large barrier for an antagonistic salt ($\Delta u^+ = -\Delta u^- = 6$, dashed-dotted curve). Here, $n_0 = 20 \text{ mM}$, $\phi_0 = 0.5$, $\Delta T = 21.5 \text{ K}$, $R = 1 \mu\text{m}$, and $A_H = 1 \times 10^{-20} \text{ J}$.

In conclusion, the theory predicts that significant potential barriers exist in a wide temperature and composition range and shows that neutral and charged colloids can be effectively suspended in a binary mixture by addition of antagonistic salts. It is worth noting that the specific adsorption of ions to the surface not discussed here will typically enhance the stabilization. The ion affinity to the wetting liquid will usually come hand in hand with a similar surface affinity thus enhancing the electrostatic repulsion.

The mechanism we describe is of potential use in numerous colloidal systems where currently only one solvent is employed and it is advantageous over existing methods in cases where the modification of the colloid surface chemistry is undesired. The most important requirement to achieve a stable suspension is to choose a salt in which the ions' solvation asymmetry in the mixture is large enough. We expect our results to be most beneficial for dispersing charge-free particles. For example, there have been large efforts recently in "transparent and conducting" electrodes for solar cell applications.³² In these works, graphite is typically sonicated to yield graphene sheets, and these sheets are dispersed using surfactants. Using evaporation or slow sedimentation, these sheets assemble as a thin and conducting layer on top of a transparent substrate. In those works, surfactants stay between graphene sheets and reduce the conductivity immensely. In this and other cases, using salts for the dispersion instead of surfactants could increase markedly the conductivity of the film.

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polynomials, the experimental solvation energy for antagonistic salts. For this more complex model, our results remain qualitatively the same and quantitatively similar.

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