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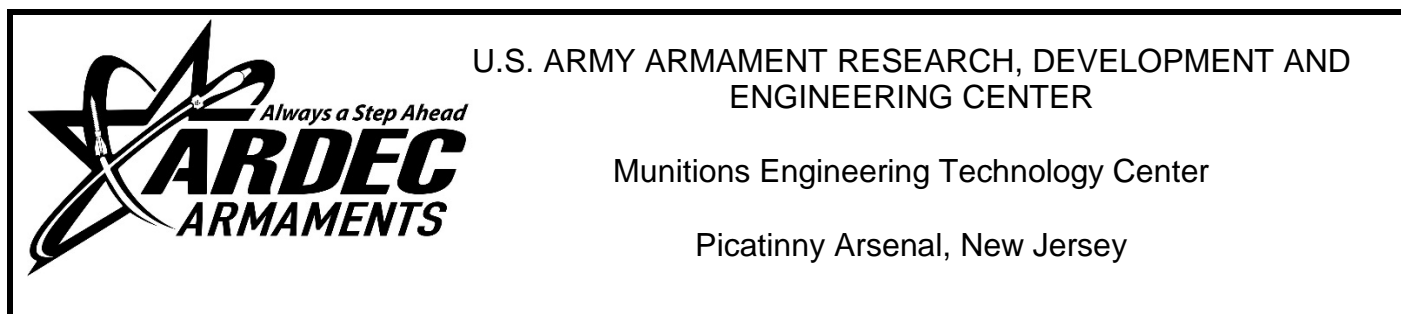
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Technical Report ARMET-TR-16027

**NANO-RDX ELECTROSTATIC STABILIZATION MECHANISM INVESTIGATION
USING DERJAGUIN-LANDAU AND VERWEY-OVERBEEK (DLVO) THEORY**

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January 2017



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14. ABSTRACT This work investigates the electrostatic stabilization mechanism of 1,3,5-trinitroperhydro-1,3,5-triazine (Nano-RDX) suspensions at different electrolyte concentrations using Derjaguin-Landau and Verwey-Overbeek (DLVO) Theory. The van der Waals attractive forces were computed at different Nano-RDX crystal sizes and showed that those forces increased at smaller crystal sizes because of an increase in surface area. The electrical repulsion force was also computed with the thickness of the double layer (Debye length) and showed that the force decay increased with ion concentration. The thickness of the double layer is reduced significantly at greater ionic strengths. Finally, the total interaction energy was calculated as a function of electrolyte concentration and predicts that 100 nm Nano-RDX particles could be stable at low concentration of 0.001 mole/l and unstable at 0.1 mole/l. The DLVO theory could serve as a basic framework to study the electrostatic stability of Nano-RDX suspensions at different electrolyte concentrations.					
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CONTENTS

	Page
Introduction	1
Derjaguin-Landau and Verwey-Overbeek Theory	1
Van der Waals Attractive Forces	1
Electrical Double Layer Repulsion Forces	2
Total Interaction Force	5
Conclusions	8
References	9
Distribution List	11

FIGURES

1 Van der Waals attractive forces for different Nano-RDX sizes	2
2 The electric double layer illustration (ref. 6)	3
3 Effect of 1:1 electrolyte concentration on the Nano-RDX electrical double layer forces	4
4 Effect of 1:1 electrolyte concentration on the Nano-RDX total interaction energy	5
5 Effect of 1:1 Electrolyte Concentration on the Nano-RDX Interaction Energy curves	6

INTRODUCTION

Nanocrystals of energetic materials exhibit enhanced performance, insensitivity, and mechanical strength in comparison to conventional coarse energetics. While processing methods are currently capable of pound scale production, one of the key remaining challenges for nanocrystals is agglomeration during processing. The interaction forces between nanoparticles in all suspensions play an important role in determining the stability of the nanocrystals. In the 1940s, Derjaguin-Landau and Verwey-Overbeek (DLVO) developed a theory to account for those interaction forces that could provide a basic framework to study the stability of the 1,3,5-trinitroperhydro-1,3,5-triazine (Nano-RDX).

DERJAGUIN-LANDAU AND VERWEY-OVERBEEK THEORY

The DLVO theory (refs. 1 and 2) is built on the assumption that the stability of colloids is determined by two main interaction forces, the van der Waals attractive forces V_a and the electric double layers repulsive forces V_r . The DLVO theory suggests that the stability of a colloidal system is determined by the sum of these van der Waals attractive (V_a) and electrical double layer repulsive (V_r) forces that exist between particles as they approach each other:

$$V_{total} = V_a + V_r \quad (1)$$

This theory proposes that the stability of a colloidal system is determined by competition between the van der Waals attraction and electrostatic repulsion forces.

Van der Waals Attractive Forces

There are three different possible origins for van der Waals forces: (1) permanent dipole-permanent dipole (Keesom) forces, (2) the permanent dipole-induced dipole (Debye) interactions, and (3) transitory dipole-transitory dipole (London) forces. The first two are very short range interactions, but the London forces are longer range attractions. Since only London forces contribute to the long-range attraction between colloidal particles, the magnitude and range of the van der Waals-London attraction are decisive in determining strategies for stabilizing colloid particles.

The van der Waals energy for two interacting spheres of radius r separated by distance h was computed by Hamaker (ref. 3):

$$V_a = - \frac{A_{12}r}{12h} \quad (2)$$

where A_{12} is the Hamaker constant. The Hamaker constant could be easily computed from the Tabor-Winterton (refs. 4 and 5) approximation for RDX in water as a case study:

$$A_{12} = \frac{3}{4} k_b T \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^2 + \frac{3h\omega_e}{16\sqrt{2}} \frac{(n_1^2 - n_2^2)^2}{(n_1^2 + n_2^2)^{3/2}} = 1.78 \times 10^{-20} \text{ J} \quad (3)$$

where n_1 and n_2 are the index of refraction of RDX and water. ω_e is the electronic relaxation frequency which is assumed to be constant for all materials, ϵ_1 and ϵ_2 are the dielectric constants of RDX and water at 5 MHz.

Figure 1 shows the calculated van der Waals force from equation 1 for different Nano-RDX crystal sizes. We can easily see from figure 1 that the van der Waals force increases for small crystal size due to their larger surface area.

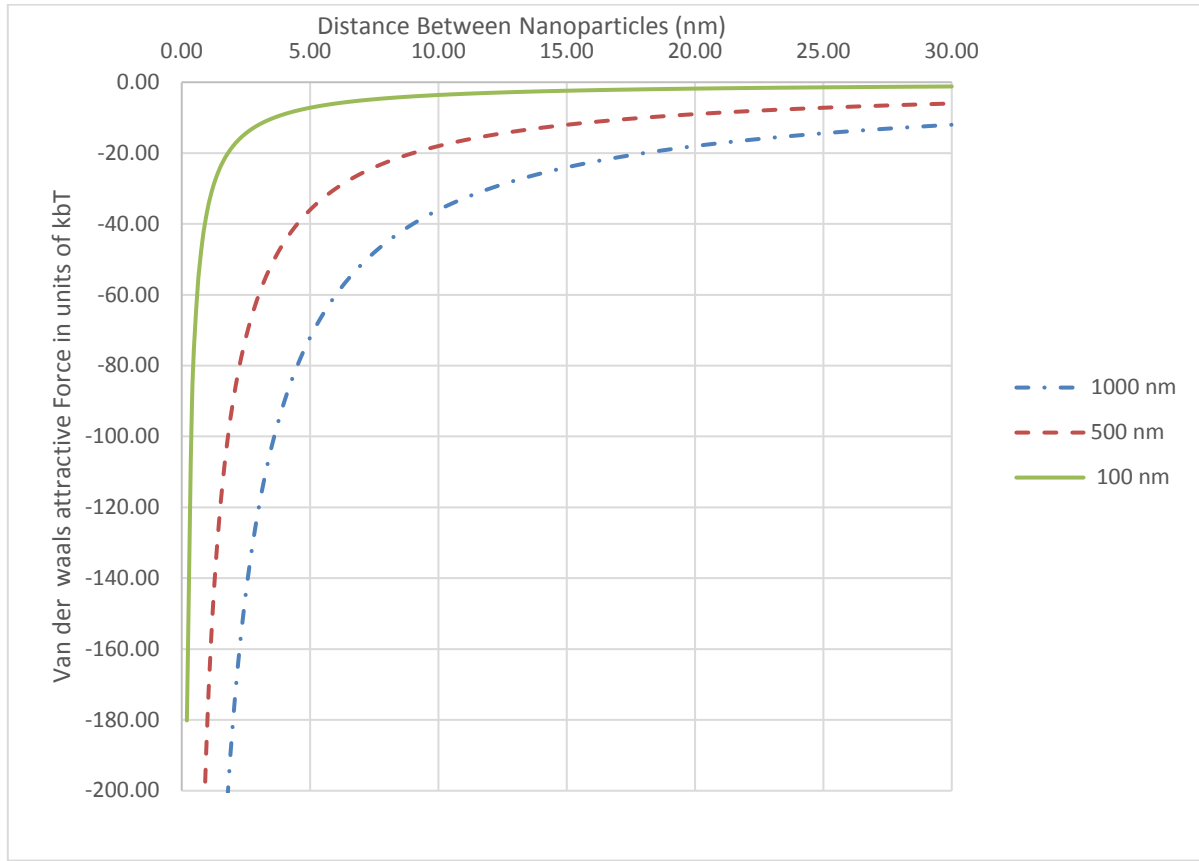


Figure 1
Van der Waals attractive forces for different Nano-RDX sizes

Electrical Double Layer Repulsion Forces

Nanocrystals in water or in any liquid of high dielectric constant usually develop surface charges, due either to dissociation of chemical groups on the surface or by physical adsorption of ions from the electrolyte. To maintain electro-neutrality, an equal number of counter ions with the opposite charge will surround the colloidal particles and give rise to overall charge-neutral double layers. A diagram of a particle in solution with an electric double layer can be seen in figure 2.

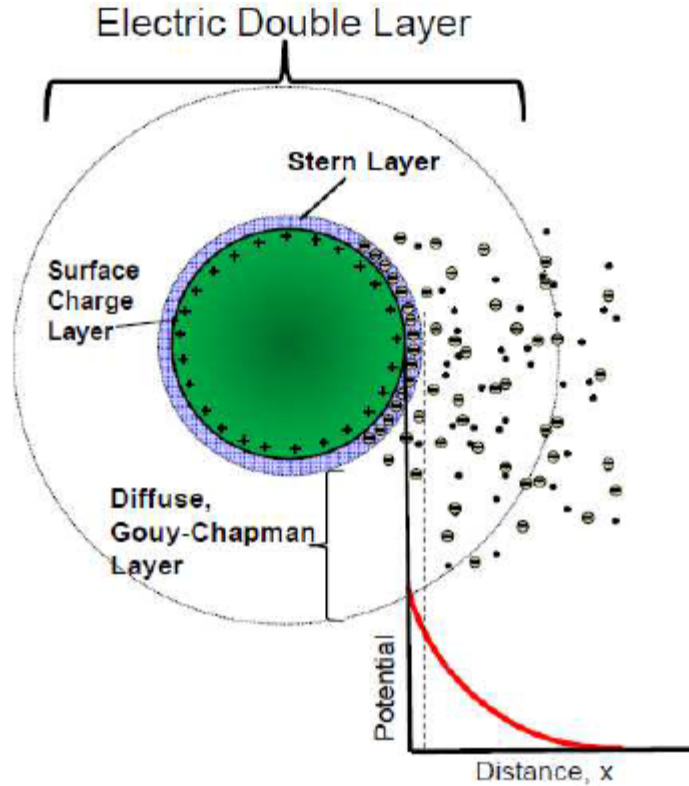


Figure 2
The electric double layer illustration (ref. 6)

The liquid layer surrounding the particle exists as two parts: an inner region (Stern layer) where the ions are strongly bound and an outer (diffuse Gouy-Chapman Layer) region where they are less firmly associated. Generally, the larger the radius of the electrical double layer is, the more dispersed the crystals. Thus, if the electric potential associated with the double layer is sufficiently high, the electrostatic repulsion between the particles prevents agglomeration. The electrostatic double-layer interactions can be estimated by means of the well-known Hogg-Healy-Fuerstenau formula (ref. 7), given by:

$$V_r = 2\pi e_0 \varepsilon r \varphi^2 \ln \left(1 + e^{-\frac{h}{\kappa^{-1}}} \right) \quad (4)$$

Where e_0 is the permittivity of free space, ε is the solution dielectric, φ is the nanoparticle potential surface, h is the distance between two spherical nanoparticles, and κ is the reciprocal of the Debye length. Debye length which represents the thickness of the double layer is given by (ref. 8):

$$\kappa^{-1} = \sqrt{\frac{e_0 \varepsilon k_e T}{2 N_a e^2 I}} \quad (5)$$

Where e is the electron charge and I is the ionic strength of the electrolyte solution.

In an electrostatic-regulated system, the degree of dispersion is controlled by adjusting the ionic strength. Salts can be added to the solution, and their ions can be adsorbed onto the particle surface to change the particle's net surface charge by modifying the electric double layer (ref. 9).

Figure 3 shows the calculated electrical repulsion force from equation 4 for 100nm Nano-RDX. As we can see from the figure, the decay increases with ion concentration, because there are more counter ions available to cancel the surface potential.

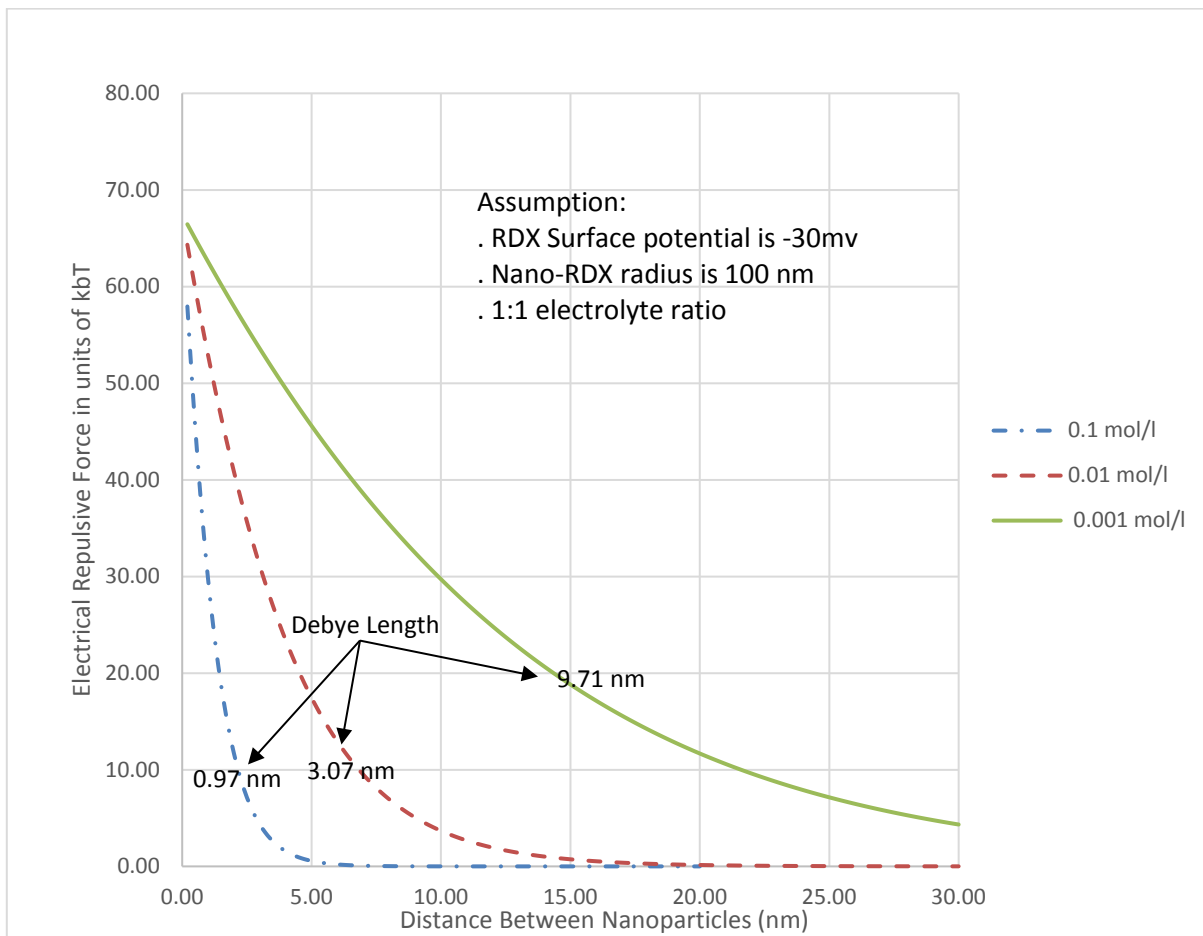


Figure 3

Effect of 1:1 electrolyte concentration on the Nano-RDX electrical double layer forces

The thickness of the double layer (Debye length) is reduced significantly with increasing ionic strength. At low ionic strengths (0.001 mol/L), the thickness of the double layer is about 9.71 nm, which is the same order of magnitude as the van der Waals attraction (fig. 1). At ionic strengths (0.1 mol/L), the thickness is less than 1 nm. In that case, the range of double layer electrostatic repulsion is usually insufficient to counterbalance the van der Waals attraction. This accounts for the fact that most charge stabilized dispersions coagulate when increasing the ionic strength of the dispersion. However, there is a trade off when adding ions to a solution. If more ions are added to a solution, then the ionic strength of the solution increases to a larger value. As the ionic strength increases, the thickness of the electric double layer shrinks, which increases the likelihood that particles will collide and agglomerate.

Total Interaction Force

The stability of a Nano-RDX system is determined by the sum of van der Waals attractive (V_a) and electrical double layer repulsive (V_r) forces. The total calculated interaction energy from equation 1 is shown as a function of electrolyte concentration in figure 4. Each individual interaction energy curve for each concentration is shown in figure 5, showing both the electrical double layer repulsive and van der Waals attractive forces. It is quite clear from figures 4 and 5 that depending on the electrolyte concentration, different phase behaviors may occur: (a) At concentration 0.001 m/L, surfaces repel strongly, small Nano-RDX (200 nm) particles remain stable with a maximum total energy of $40 k_bT$. If that barrier is greater than $20 k_bT$, it is generally assumed that there is not enough Brownian motion to force the Nano-RDX to agglomerate due to van der Waals attraction forces. The thickness of the electrical double layer is around 10 nm. (b) At concentration 0.01 m/L, the maximum total energy is around $22 k_bT$ and it get below the barrier of $20 k_bT$ at 3 nm distance which correspondent to the thickness of the electrical double layer. This concentration could be considered as the border line between the stability and instability of Nano-RDX. (c) At concentration 0.1 m/L, the van der Waals attraction force is dominant. This explain why most charged nanoparticles agglomerate when increasing the electrolyte concentration of the dispersion.

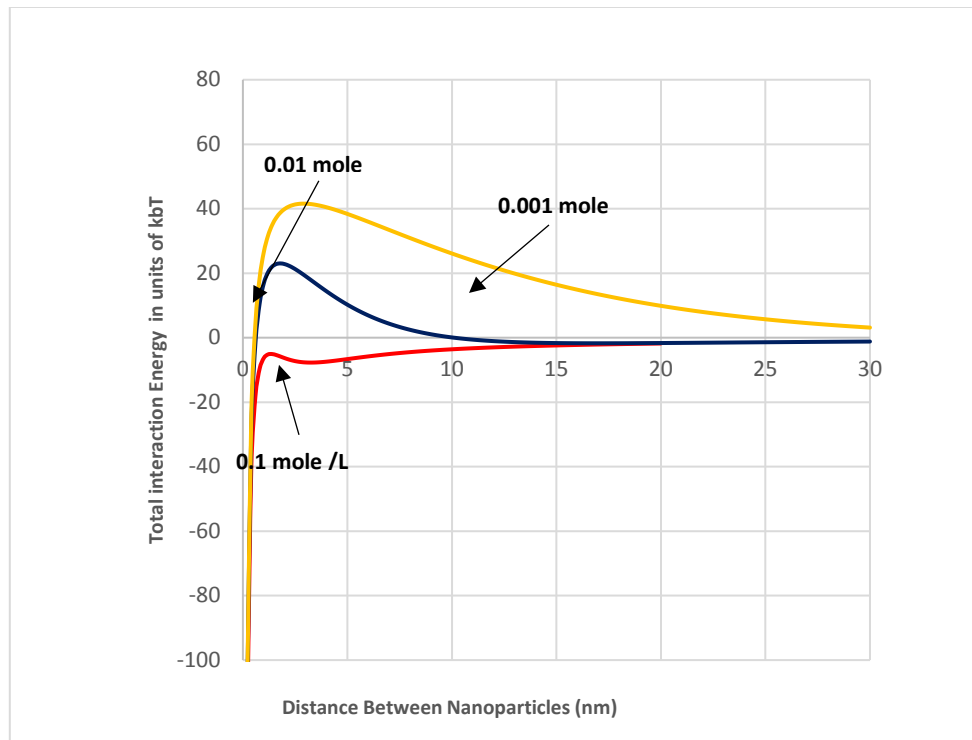
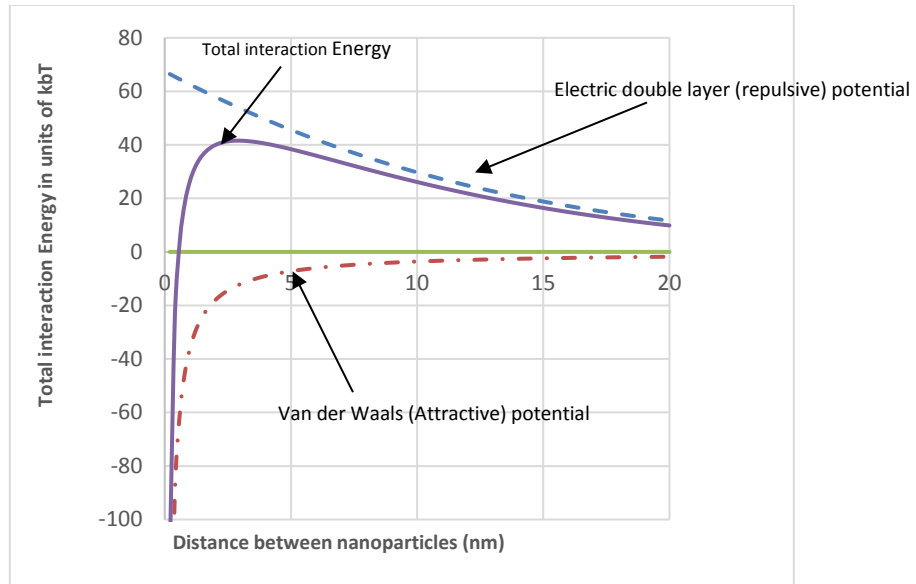
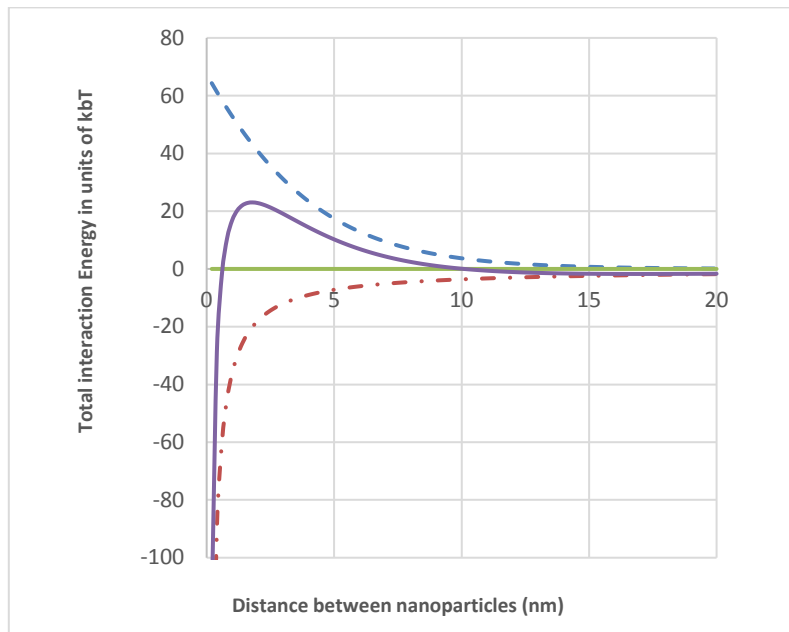


Figure 4
Effect of 1:1 electrolyte concentration on the Nano-RDX total interaction energy

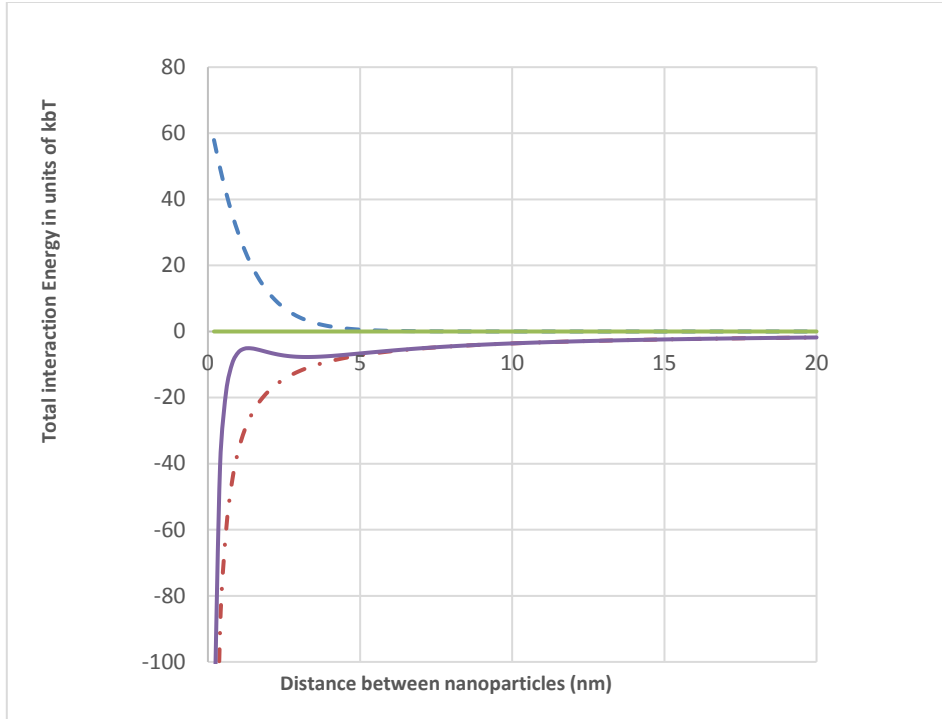


(a)
0.001 mole/L



(b)
0.01 mole/L

Figure 5
Effect of 1:1 Electrolyte Concentration on the Nano-RDX Interaction Energy curves



(c)
0.1 mole/L

Figure 5
(continued)

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CONCLUSIONS

Derjaguin-Landau and Verwey-Overbeek (DLVO) theory predicts that 100nm Nano-RDX particles could be stable at concentrations as low as 0.001 mole/L and unstable at 0.1 mole/L. The surface potential charge of Nano-RDX is assumed to be -30 mv, but this value must be confirmed experimentally. DLVO theory could serve as a basic framework to study the electrostatic stability of Nano-RDX at different electrolyte concentration. This stabilization could be easily regulated by adjusting the salt concentration in the Nano-RDX solution, making it cost effective and easily implemented.

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