Study of Contributions of Hydrodynamics and Surface Forces to Controlled Particle Deposition

Majid Bahmani-Makvandzadeh
Department of Chemistry, Tarbiat Moalem University, Dr. Mofateh Street, Tehran, Iran.

ABSTRACT
Design of an electrochemical adsorption cell utilising Reticulated Vitreous Carbon [RVC] as the working electrode, stainless steel as the counter electrode and a cellulose acetate membrane separator for the separation of 5.4 \( \mu m \) polystyrene latex colloidal particles from a KCl solution is described. Effect of variation of flowrate and electrolyte concentration on the rate of deposition is investigated and the results are compared with Derjaguin-Landau-Verwey-Overbeek [DLVO] predictions for the occurrence of favourable and unfavourable deposition conditions.

Keywords: Particle Deposition, Polystyrene Latex, DLVO Theory

Theoretical Background
Deposition of colloidal particles onto a substrate is encountered in a variety of natural processes such as particulate fouling of heat exchangers, thrombus formation in vascular prostheses and other artificial organs and aerosols entering the lungs. Deep bed filtration of waste waters is perhaps the most prominent example of importance to industry.

Theories utilised in the literature for deposition of colloidal particles onto substrates stem from the theories on the stability of colloidal suspensions. The contributions by Verwey and Overbeek [1] and by Deryaguin and Landau [2] set out the underlying foundation for the modern colloid science. The Deryaguin-Verwey-Landau-Overbeek (DLVO) theory assumes that the forces operating between colloidal particles in suspension comprise the electrostatic double layer and the attractive van der Waals and the sum of these two forces constitute the total force keeping colloidal particles in suspension.

![Figure 1. Variation of Interaction Energy with Distance for Two Surfaces](image-url)
Once a colloidal particle is in the vicinity of a charged surface, a total interaction energy between the surfaces of the type shown in Figure 1 could result. The primary minimum presents a deep energy well and a particle in the primary minimum is held irreversibly. Prior to deposition in the primary minimum, an energy barrier must be surmounted.

Ninham [3] provides a history of development of the DLVO theory and states that the major underlying assumptions of the DLVO theory of colloidal stability are:

1. The surfaces are molecularly smooth and solid. They are inert except in so far as they provide a source of counterions that live behind charged surfaces.
2. An intervening solvent water for an electrolyte has bulk liquid properties up to the interface.
3. Electrical double layer and van der Waals forces are treated independently and are assumed additive.
4. The boundary conditions for the double layer are constant charge or constant potential.
5. The double layer interaction potential is computed using the non-linear Poisson-Boltzmann equation for point ions. Discreteness of charge effects are taken into account by a smeared out surface charge approximation. This can be shown to be a good approximation at very low, and very high electrolyte concentrations, but poses difficulties at intermediate ranges, typically $10^{-3}$ to $10^{-1}$ M.
6. The opposing attractive van der Waals forces between the plates is calculated on the assumption that an intervening liquid has a uniform density and orientation profile. It is obtained by pairwise summation of London-van der Waals forces.

Predictions based on the DLVO theory suggest the occurrence of favourable and unfavourable deposition conditions when overall attractive and repulsive energies exist between surfaces, respectively. Indeed, many experimental results in the literature confirm the occurrence of favourable and unfavourable deposition conditions [4-8]. However, the DLVO theory suffers from a few shortcomings [4, 8, 9]. Weiss, et al. [10] state that previous works indicate that the theoretical predictions based on the DLVO theory under unfavourable deposition conditions predict a sudden drop in the rates of deposition, whereas experimental results indicate a gradual decrease in the rate of deposition. To account for this discrepancy, a few ideas have been put forward. For example, inclusion of other forces such as Born repulsion and the so-called structural forces such as hydration, hydrophobic and steric interactions has resulted in the extended-DVLO theory.

Another idea put forward for this discrepancy has been to include the effects of surface roughness and charge heterogeneity. Shellenberger, et al. [11] carried out deposition of bacteria on glass beads in a packed bed which had been treated previously to obtain different surface roughnesses. Surface roughness on glass beads was measured by an atomic force microscopy. The deposition experiments revealed that glass beads with more surface roughness produced less deposition of bacteria.

Adamczyk, et al. [12] investigated the effect of surface charge heterogeneity on the rate of deposition in an impinging cell using mica sheets as the substrate and polystyrene latex as the colloids. It was concluded that substrates with higher surface charge heterogeneity produced more deposition.

Chen, et al. [13] carried out experiments to study the effect of surface charge heterogeneity on the rate of deposition in a packed bed and concluded that the mean value of the charge heterogeneity rather than its spatial distribution in the bed influenced the rate of deposition in the bed.

Effect of hydrodynamic shear rate on detachment of deposited colloids, has been studied experimentally in a packed bed by Bai and Tien [14]. They reported that high detachment rates were obtained at high flowrates and also they noted even higher rates of detachment with fluid flow shock.

Bergendahl and Grasso [15] carried out experiments for the detachment of colloidal particles in a packed bed and at a flowrate of 75 ml/min. They obtained 50% detachment of deposited particles. They also obtained relationships that could predict the rate of detachment.

**Estimation of Electrostatic Forces**

Adamczyk [16] in a review paper states that deposition of colloidal particles onto a substrate takes place in two stages: (1) transport stage, wherein the particles are brought into the vicinity of the collector by bulk fluid flow or diffusion; and (2) attachment process, wherein the particle
is physically deposited and held in place by electrostatic forces. In the theoretical section of this work it will be assumed that the main forces contributing to adsorption interaction between the surfaces will be due to electrical double layer and van der Waals attraction.

Adamczyk, et al. [12] provide an overview of the role of electrostatic forces in the deposition process and also present common approaches for the estimation of London-van der Waals and electrical double layer forces.

The London-van der Waals force is an attractive force exerted by all atoms and or molecules, polar or not. They arise from the fluctuation in the electrical charge distribution around atoms or molecules. These fluctuations produce an instantaneous dipole so that one molecule in the neighbourhood of another experiences attraction. There are basically two approaches for the estimation of London-van der Waals force. One is due to Hamaker [18], in which the attractive energy between two particles is calculated as the pairwise summation of all the intermolecular interactions. The second approach is based on the Lifshitz [19] theory, which attempted to overcome the inadequacies of the Hamaker approach, by calculating the attractive energy in terms of the bulk properties of the particle and the intervening material. In both approaches a value for the Hamaker constant, A, having units of energy is required.

If the distance between atoms is larger than 50 nm, by the time the electric field from one atom has reached and polarised the other, the electron configuration of the first atom will have changed. There will be poor interaction between the dipoles and atoms experience what is called the “retarded” London-van der Waals attraction energy. Therefore, calculation of the London-van der Waals attractive energy falls into two categories:

1. At separation distances greater than 50 nm, where retarded London-van der Waals is in operation.
2. At separation distances less than 10 nm, where particles experience non-retarded London-van der Waals attraction.

In this work, the expression by Gregory [20] for retarded interaction was used for estimation of van der Waals energy. A value of 1.7× 10⁻²⁰ J was used for the Hamaker constant, A, for polystyrene-water-carbon.

\[ V_r = -\frac{A}{12h} \left( 1 - \frac{h\omega}{\omega} \right) \ln \left( 1 + \frac{\omega}{h\omega} \right) \]  \hspace{1cm} (1)

where \( h = 5.32 \), and \( \omega = 100 \text{ nm} \) is the characteristic wavelength.

Jia and Williams [21] state that most substances exhibit a surface electric charge when immersed in a polar (e.g., aqueous) medium and possible routes for charge transfer could be ionisation, ion adsorption and ionic dissolution. This surface charge forces the distribution of nearby ions in the polar medium to achieve electroneutrality. Ions of opposite charge are attracted towards the surface and ions of like charge are repelled away from the surface. This together with the mixing tendency of thermal motion leads to the formation of an electrical double layer made up of the charged surface and a neutralising excess of counter ions in the polar medium.

The starting relationship for estimation of the electrical double layer is the non-linear Poisson-Boltzmann equation for the distribution of potential around a body:

\[ \psi \approx -\frac{4\pi \varepsilon}{\kappa} \sum_i Z_i n_i \exp \left( \frac{-Z_i e \psi}{kT} \right) \]  \hspace{1cm} (2)

Adamczyk and Wieronski [17] provided a review of latest information on electrical double layer estimation and state that due to the non-linearity of the Poisson-Boltzmann equation, the only analytical solution available is for the interaction of two planes and an analytical solution for the important case of sphere-sphere interaction has not yet been achieved. When two surfaces approach each other their electrical double layers overlap and if the electrical double layers restore equilibrium quickly, then the surface potentials of the surfaces will be assumed constant and on the other hand, if electrical double layers restore equilibrium slowly, then the interacting surfaces are assumed to have constant charges during interaction.

The sphere-plane expression by Ruczenie and Prieve [22] was used for the estimation of electrical double layer interaction:

\[ V_{r_p} = \varepsilon \left( \frac{kT}{e} \right)^2 \left( \tanh \left( \frac{\varepsilon \psi_1}{4kT} \right) \tanh \left( \frac{\varepsilon \psi_2}{4kT} \right) \exp (-k\kappa) \right) \]  \hspace{1cm} (3)

\( \kappa \) is called the Debye-Huckel reciprocal length and is defined as:

\[ \kappa^2 = \frac{e^2}{\varepsilon kT} \sum_i Z_i n_i \]  \hspace{1cm} (4)
This parameter is very important for the quantitative description of electrical double layer and is often (but imprecisely) regarded, whereas the ‘thickness’ of the double layer. A high electrolyte concentration leads to a compact electrical double layer and a low electrolyte concentration leads to a thick electrical double layer.

**Zeta Potential**

Shaw [23] discusses the electrokinetic phenomena and states that a colloidal particle, in solution, is enveloped by an imaginary surface of shear that lies close to the surface and within which the fluid is stationary. In electrophoretic mobility measurement a particle placed in an electric field moves along with the fluid in its surface of shear. Measurement of electrophoretic mobility will provide an estimate of the zeta potential, potential at the surface of shear, of the particle. In non-aqueous solution following measurement of the electrophoretic mobility, \( u_e \), the zeta potential can be estimated from the equation derived by Hückel:

\[
 u_e = \frac{2 \varepsilon \zeta}{3 \mu} \tag{5}
\]

For aqueous solutions the equation by Smoluchowski is utilised:

\[
 u_e = \frac{\varepsilon \zeta}{\mu} \tag{6}
\]

In this work, zeta potentials of polystyrene latex particles and the carbon substrate were measured using ZetaPlus (Brookhaven Instruments Corporation, USA). The menu-driven interface programme of ZetaPlus allowed measuring electrophoretic mobilities and the consequent conversion, by the programme, of the mobilities into zeta potential values using the Smoluchowski’s equation.

**Apparatus and Experimental Set-up**

Elimelech et.al. [4] discuss the deposition studies in the literature and point out that ideal collectors and particles are usually used for investigation of deposition processes. Ideal particles are smooth, spherical, and monodisperse with narrow size distributions. Ideal collectors used are parallel plate, stagnation point flow, bed of glass beads and these provide hydrodynamics and interaction energies that can be described within the existing framework.

In this study, polystyrene latex particles of median size 5.4 \( \mu \)m were used as the colloidal particles and Reticulated Vitreous Carbon (RVC) purchased from Electrosynthesis (NY, USA) as the deposition medium. RVC is an open pore material with a honeycomb (foam) structure and it has a bulk void volume of 97%. Fig. 2 shows an SEM photograph of the RVC.

![Figure 2. SEM Photograph of Reticulated Vitreous Carbon](image_url)
Zeta potential values and signs are measures of the surface charge carried by the particles. Figs. 3 and 4 show variation of the zeta potential with pH and electrolyte concentration (KCl) for the polystyrene particles and RVC, respectively. It can be seen that RVC shows relatively higher zeta potential values compared to the polystyrene latex particles at the same pH and KCl concentration.

The point of zero charge for both polystyrene latex and RVC is not obtained in this range of pH and electrolyte concentration. Variation of electrolyte concentration has a more pronounced effect on zeta potential values of the RVC.

Fig. 5 shows a schematic representation of the cell designed for the experiments. The cell was made of a Perspex acrylic sheet of 7mm thickness. The working electrode was a slab of RVC 60.0 mm long, 25 mm thick and 50 mm wide. The counter electrode was a piece of stainless steel plate screwed onto the face opposite to the working electrode. The working electrode was separated from the counter electrode by means of a cellulose acetate membrane, having a pore size of 1.0 μm, encased between two Perspex slabs. A Calomel reference electrode was used for measurement of the applied potentials. The potentials were applied to the working electrode (RVC) by means of a potentiostat which was interfaced to a PC. The KCl electrolyte and the polystyrene latex particle feed suspensions were delivered using two

**Figure 3.** Variation of Polystyrene Latex Particles Zeta Potential with pH and KCl Concentration

**Figure 4.** Variation of RVC Zeta Potential with pH and KCl Concentration

**Figure 5.** Schematic Representation of the Electrochemical Adsorption Cell: 1: inlet, 2: top perspex cover, 3: perforated upper distributor, 4: area for RVC slab, 5: hole for wire connecting RVC slab to potentiostat, 6: membrane, 7: bottom perforated plate, 8: bottom perspex cover, 9: outlet pipe, 10: perspex membrane carrier, 11: stainless steel counter electrode, 12: 'side arm' for reference electrode, 13: hole for insertion of reference electrode
peristaltic pumps and these were mixed before entering the cell. The inlet and outlet particle number concentrations were measured by a portable turbidimeter (model 6035, Jenway Equipment Ltd.). A typical experiment started with equilibration stage, wherein only KCl electrolyte solution was passed through the cell, using a Watson-Marlow peristaltic pump, until outlet conductivity and pH, cell voltage and current and also the RVC electrode potential remained constant. At this point, the polystyrene latex particles were introduced into the KCl stream using a peristaltic pump until the feed particle number concentration was within the range 0.51-0.97 x 10^6 particles/cm^3. The time for the introduction of latex suspension was noted and this was taken as the zero on the time-axis for the particle break-through curves. Throughout an experiment the cell voltage and current, RVC electrode potential, pH at inlet and outlet, and conductivity were measured.

Results and Discussion

It was mentioned that the deposition process consists of two main stages, i.e., transport and deposition stages. The transport stage may occur by bulk fluid flow, interception, sedimentation

under the influence of gravity, inertial impaction and diffusion. For non-Brownian particles the diffusion process becomes negligible, compared to the bulk fluid flow. The polystyrene latex particles used in this study were 5.4 μm in diameter and hence, effect of diffusion becomes negligible. For reasonably low flow rates, Re<1, inertial impaction is usually assumed negligible compared to the bulk flow. The highest particle Reynolds number employed in this study was 2.8x10^3 and hence the contribution due to inertial impaction can be ignored. Therefore, only the effect of gravity and electrostatic forces need to be considered in any theoretical analysis of the experimental results. Once the particles are in the vicinity of the collector they are firmly held in place by the action of electrostatic forces. In order to observe solely the effect of these forces the effect of hydrodynamic interactions has to be kept at a minimum. Therefore, experiments carried out were directed mainly at finding out the dividing line between hydrodynamically-controlled and electrostatically-controlled processes. Indeed, if the surface force-controlled regime can be established, then it may be possible to control the rate of deposition/desorption of particles by simply varying the surface forces.

The highest volumetric flowrate used in these experiments was 34 cm^3 min^-1 and at this
flowrate the RVC potential was varied to observe any change in the rate of deposition. Fig. 6 shows the interaction energy profiles and the experimental particle break-through curves at this flowrate. Run Ex2 was carried out with no applied potential to the RVC. The latex particles and the RVC have zeta potential values of −8.5 mV and −26.5 mV, respectively, at this KCl concentration and pH. The solid line in the energy profile shows the presence of repulsive forces between particles and collector and furthermore, the height of energy barrier is estimated to be more than 15 kT. An energy barrier more than 15 kT is considered to be insurmountable by the particles and no deposition of particles is expected to occur. Applying a potential of −200 mV vs. Standard Calomel Electrode (SCE), to the collector in run Ex3, as seen in the energy profile, should theoretically increase the repulsive forces between the particle and collector, and hence, a faster break-through of the particles should occur, compared to run Ex2. Increasing the RVC potential to −300 mV, in run Ex4, further increased the height of energy barrier and theoretically less deposition of particles should have occurred.

Run Ex5 was carried out with +300 mV applied to the RVC and as can be seen in energy profile, no energy barrier exists between particles and collector and attractive forces are present and theoretically speaking, a lot of deposition should have occurred. Comparing the particle break-through curves for these experiments, it can be seen that no observable variation in the rate of deposition happens and indeed, even when a positive potential is applied to the collector, still no differentiation of break-through curves is possible and complete break-through of particles occur approximately after 350 s in all experiments. It can be concluded from these results that at this volumetric flowrate and KCl concentration the effect of surface forces is negligible compared to hydrodynamics. Figure 7 shows the experimental results for the same KCl concentration and pH as before but at a lower flowrate of 5.6 cm² min⁻¹. It is hoped that at this lower flowrate the contribution of hydrodynamics to deposition becomes less and hence, the contribution of surface forces becomes observable. At a collector potential of −300 mV, unfavourable deposition condition prevails and low deposition is expected and similarly at +300 mV favourable deposition condition is predicted and hence, high deposition is expected. In contrast to the previous results, observable

![Figure 7. Particle Break-through Curves at KCl Concentration of 0.0001 mol dm⁻³, Volumetric Flowrate of 5.6 cm² min⁻¹ and RVC Potential Shown in the Inset](image-url)
differences between favourable and unfavourable deposition conditions can be observed and steady state values of 0.88 and 0.8 for the unfavourable and favourable conditions, respectively, further justifies the conclusion.

![Graph](image)

**Figure 8.** Particle Break-through Curves at KCl Concentration of 0.001 mol dm$^3$, Volumetric Flowrate of 1.7 cm$^3$ min$^{-1}$ and RVC Potentials as Shown in the Inset

Following from the results of the experiments just discussed, several other experiments were carried out at an even lower flowrate of 1.7 cm$^3$ min$^{-1}$ to arrive at conditions, wherein the surface forces can be controlled by means of varying the collector potential. Fig. 8. shows the particle break-through curves at a KCl concentration of 0.001 mol dm$^3$ and a flowrate of 1.7 cm$^3$ min$^{-1}$. Fig. 9. shows the corresponding particle-collector interaction energies predicted for the experimental conditions shown in Fig. 8. From Fig. 9, it is predicted, from DVLO theory according to the prediction of occurrence of favourable or unfavourable deposition conditions, that deposition should occur, in the order Ex10 > Ex15 > Ex16 > Ex13 > Ex14 > Ex11 > Ex12, that is, from the most favourable to the least favourable deposition conditions.

Table 1. shows the weight ratios of particles deposited for these experiments. From the figures in table 1. and the particle break-through curves it can be concluded that the deposition in fact occurs as Ex12 > Ex13 > Ex16 > Ex15 > Ex14 > Ex11 > Ex10. With the exception of Ex12 and Ex10, it may be said that generally speaking, variation of RVC potentials potentiostatically proves successful in the sense that results can be distinguished according to the occurrence of favourable and unfavourable deposition conditions.
Oren, et al. [24] carried out deposition experiments of 0.15 μm latex particles onto 10 μm graphite felt. They varied the potentials in a wide range of −500 to +500 mV to allow study of colloidal adsorption under the condition of double layer charging and when water electrolysis occurred.

They observed that when potential was +500 mV, pH decreased followed by a decrease of colloidal concentration, and when potential was changed to −500 mV, pH and particle concentration increased. They concluded that due to the high surface area of electrodes at these high overpotentials some redox reactions occur and these can change the pH of the solution and this in turn changes the surface charge of particles and consequently the adsorption rates change.

---

**Table 1. Total weight and normalised weight of particles deposited**

<table>
<thead>
<tr>
<th></th>
<th>Ex10</th>
<th>Ex11</th>
<th>Ex12</th>
<th>Ex13</th>
<th>Ex14</th>
<th>Ex15</th>
<th>Exc16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of Feed Entered (WFT), × 10^{-3} g</td>
<td>4.78</td>
<td>6.25</td>
<td>6.99</td>
<td>6.54</td>
<td>5.44</td>
<td>7.13</td>
<td>6.32</td>
</tr>
<tr>
<td>Weight of Particles Deposited (WT), × 10^{-5} g</td>
<td>0.08</td>
<td>0.56</td>
<td>3.48</td>
<td>2.62</td>
<td>0.90</td>
<td>2.25</td>
<td>1.95</td>
</tr>
<tr>
<td>WT/WFT (× 10^{-3})</td>
<td>0.17</td>
<td>0.89</td>
<td>4.90</td>
<td>4.00</td>
<td>1.67</td>
<td>3.16</td>
<td>3.08</td>
</tr>
</tbody>
</table>
To investigate the findings by Oren, et al. [24], run pH was carried out at a higher potential of 417 mV for the RVC. At this potential, a change in the pH of the solution due to redox reaction is reported. Indeed, plot (c) in Fig. 10. shows that the observation made by Oren, et al. [24] is well justified, i.e., at high negative potentials due to evolution of hydrogen the pH rises from 6.2 to 9.4. After equilibration period of 4200 s, the feed suspension was introduced into the column as seen in plot (c) and from this point on the pH reduced to 7.0. Fig. 11. shows the particle breakthrough curve for this run (note that time=0 in this plot is equal to time=4200 s in Fig. 10.) and it can be seen that upon the

![Figure 11. Particle Break-through Curves at High Collector Potential](image-url)
termination of the interface program, the RVC potential slowly returns towards its rest potential of +45 mV. DLVO theory suggests that the more positive the RVC potential the more attractive the forces between the particle and collector, leading to theoretically higher deposition occurring. From Fig. 11. It can be seen that, this is confirmed experimentally since upon termination of the potentiostatic program there seems to be more deposition occurring.

Conclusion
For the present experimental conditions the main forces contributing to the deposition process are the surface forces and hydrodynamics. At the highest flow rate of 34 cm² min⁻¹, the electrostatic forces were shown to be negligible compared to the hydrodynamics. Indeed, the effect of surface forces at the KCl concentration of 0.001 mol dm⁻³ apparently only became significant at a flow rate of 1.7 cm³ min⁻¹. At this flow rate and KCl concentration of 0.001 mol dm⁻³, the experimental results show clear evidence of conditions governing the occurrence of favourable and unfavourable deposition conditions. The variation of collector potential under unfavourable deposition condition does not produce large changes in the deposition rate, as shown in Fig. 8, whereas variation of collector potential under favourable conditions produces significant changes in the deposition rate. At collector potentials of −300 mV vs. SCE, hydrogen evolved and this was accompanied by a rise in the pH of the solution. This rise in pH affected the zeta potential of the particles though slightly, but significantly.

Nomenclature

- \( a \): particle radius
- \( A \): Hamaker constant
- \( e \): electronic charge
- \( h \): surface to surface separation
- \( k \): Boltzmann constant
- \( n_i^b \): bulk concentration of ion I
- \( V_A, V_R \): van der Waals and electrical double layer energies
- \( T \): absolute temperature
- \( u_e \): electrophoretic mobility
- \( Z_i \): valence of the ion i
- \( \varepsilon \): dielectric constant of a medium
- \( \kappa \): Debye-Hückel reciprocal length
- \( \omega \): characteristic wavelength (100 nm)

\( \psi_1, \psi_2, \psi \): surface potentials
\( \zeta \): zeta potential
\( \mu \): fluid viscosity

References
3. B.W. Ninham, Colloid Interface Sci. 83(1999), 1-17.

Iranian Journal of Chemical Engineering, vol. 1, No. 1