

Direct measurement of the depletion interaction in binary solutions of polyelectrolytes

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Direct measurements of a depletion interaction between silica surfaces immersed in binary mixtures of non-adsorbing sodium poly(styrene sulfonate) have been made with an atomic force microscope. Variations in the secondary minimum depletion interaction as a function of binary mixture composition were recorded for a number of polymer molecular weights. The position and depth of the minimum in the force data was seen to depend on both the binary mixture composition and the choice of polymer molecular weights used in the mixture. For binary mixtures containing a low molecular weight polymer at a concentration near to or below the chain overlap concentration (C^*) the position and depth of the minimum was seen to depend strongly on the properties of this low molecular weight component. This is consistent with previous theory predictions that depletion interactions in binary polymer mixtures will be controlled by the smaller component which can reside within the depletion layer of the higher molecular weight component.

Introduction

The stability of a dispersion of micro-particles in the presence of smaller non-adsorbing polymers or particles remains an area of great scientific and technical interest. For such systems, it is now well established that flocculation of the micro-particles can be induced by the non-adsorbing species if it is at sufficient concentration through a so-called depletion flocculation mechanism.¹ The main aspects of this flocculation mechanism have been described both theoretically and from experimental investigations.² Depletion interactions are caused when a non-adsorbing solution species (polymer molecule or colloid particle) is excluded from the gap between two larger particles, as they approach one another on a collision trajectory, on the basis of its size. This exclusion leads directly to a solvent rich region between the particles; this is osmotically unfavourable and the net result is the establishment of a suction pressure that pulls the particles together and causes aggregation. The key physical features of interest are the dimensions of the soluble non-adsorbing species, since this determines the distance over which the force is active, and the overall solution concentration since this determines the magnitude of the osmotic pressure driving force. The main theoretical and practical aspects of this interaction have been studied in great detail over the last 50 years and as a result, the broad features controlling this interaction are now well understood. A number of excellent reviews are available concerning this depletion interaction and the current level of understanding.^{1,2}

In most cases, however, this earlier work has concentrated on well-characterised polymer solutions or colloid dispersions;

in particular these studies have examined depletants, whether polymers, surfactants or particles with an essentially monodisperse size distribution. In real systems, it is more common for the polymer to have a polydisperse size distribution. Despite this, there have been very few systematic studies of depletion in such systems reported in the open literature.^{3–6}

The direct measurement of depletion interactions has, until recently, proven difficult as a result of the relatively small magnitude of these forces. Initial attempts with the surface force apparatus (SFA) were not able to directly measure the interactions. Instead, the presence of the depletion interaction was inferred from the overall interaction potential energy data.⁷ The first direct measurement of depletion interactions was reported by Richetti and Kékicheff for a dispersion of wormlike micelle aggregates.⁸ Despite these early reports, the relative insensitivity of the SFA has not generally made it a favoured approach to investigate depletion forces. During the last decade, there has been considerably more interest in using either colloid probe microscopy or total internal reflectance microscopy (TIRM) approaches for measuring these forces.^{9,10} Using these techniques, researchers have confirmed the main aspects of theory predictions for the depletion interaction both in aqueous and non-aqueous systems. In aqueous systems, depletion interactions have been described for non-ionic polymers,⁹ polyelectrolytes,^{11–15} nanoparticles,⁶ and micellar aggregates.^{16–18} However, as for the earlier classical investigations, the work reported to date has concentrated mainly on essentially size monodisperse depletants.

Further details about the presence of structural interactions caused by long-range repulsive interactions between the depletants themselves, have also been reported and investigated using the same direct force balance approaches.^{12–14,17,19} Additional information about depletion and structural interactions has been obtained from studies of thin liquid films containing polyelectrolytes and particles.²⁰

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Very little published information is available concerning experimental investigations of mixtures of depletants with differing characteristic sizes. Jenkins and Vincent studied the flocculation of colloidal particles in the presence of mixtures of two molecular weights of a non-adsorbing polymer.³ Their data showed some interesting non-equilibrium effects based on how these systems were mixed. More interestingly for this work, they confirmed the theoretical predictions that in binary mixtures of polymers, it is the smaller polymer that has a stronger influence since it will always be able to locate itself inside the depletion layer of the larger polymer. In this paper, we report a study of the forces of interaction between silica surfaces in the presence of binary mixtures of a nonadsorbing polyelectrolyte [sodium poly(styrene sulfonate)]. These forces were measured using an AFM configured for use as a force balance. The data obtained are compared to standard scaling theories for salt-free polyelectrolyte solutions.

Experimental details

Materials

Reagents. Commercial standard samples of sodium poly(styrene sulfonate) [NaPSS] were used here (Polysciences, Warrington, PA). Full details of the polyelectrolytes used in this study are given in Table 1. All samples were used as supplied. A stock aqueous solution of each polymer was prepared at a concentration of 10 000 ppm and after dissolution of the polymer under gentle agitation, measurements were generally performed within 24 h. Binary mixtures of the polymer solutions were prepared from the stock solutions immediately prior to their use. All water used was distilled and then purified to Millipore Milli-Q grade. The solution pH was adjusted using stock solutions of potassium hydroxide or nitric acid (BDHChemicals, ARgrade). All measurements reported here were performed at pH 7 and at a temperature of 25 °C.

AFM probes. Data reported here were collected using commercially available silicon cantilevers (Digital Instruments) with integral tips. These cantilevers are assumed to have an inherent surface oxide layer. The radius of the tip was determined using the technique of Drummond and Senden.²¹ In this approach, the interaction forces between the probe of interest and a flat plate are measured across a solution of 1.5 mM cetyltrimethylammonium bromide (CTAB). The CTAB forms an adsorbed layer at the solid–liquid interface that has a known surface potential of 90 mV. Careful fitting of the resultant force–distance profiles using a known interaction potential and Debye length allows the radius of the probe to be extracted. All the probes were cleaned immediately prior to use by exposure to an intense UV source for about 10 min.

Silica surface. The silica surface used here was prepared by the controlled oxidation of a silicon wafer at 1000 °C in a pure oxygen atmosphere. The wafer has a surface oxide layer that is approximately 100 nm thick. The mean roughness of this plate, determined from AFM images, was found to be ± 1 nm over a $1 \times 1 \mu\text{m}$ area. The plate was cleaned immediately prior to use with a chemical treatment as described by Pagac *et al.* followed by rinsing in copious quantities of pure water.¹⁰

Force measurements with the AFM. The use of an AFM for direct force measurements on colloidal systems is an established technique. Force–distance data between the silica surfaces of interest were collected using a Nanoscope III AFM (Digital Instruments). In the force mode, the standard X – Y raster scan is suspended and the flat surface substrate is moved toward and away from the sensing cantilever probe only in the Z -direction.

In a typical experiment, one of the cantilever probes was mounted into a commercial liquid cell (Digital Instruments). The liquid cell was then mounted into the AFM head unit and this was then attached to the scanner. All of these operations were performed in a clean laminar flow hood. After the two surfaces were brought into close proximity, the solution of interest was introduced into the cell. Force data were collected after a 30 min equilibration period. Whenever the solution was changed, at least 30 min were allowed to elapse for the system to reach stability before measurements were taken. Given that the polymer was non-adsorbing, a single probe could be used for multiple measurements; in this paper, all the reported data were collected with a single probe to minimize errors when comparing between probes. However, the data reported here were verified in multiple repeat measurements with each probe and each data set was also verified using at least two different probes.

The deflection of the cantilever is monitored continuously, using a split photodiode and a reflected laser beam. Deflections are recorded as the flat surface is driven toward and away from the cantilever. These can be converted to force–distance information using the protocol of Ducker *et al.*²² Quantitative force data require an accurate knowledge of the spring constant for the cantilever probes. Spring constants were determined here using the technique of Cleveland *et al.*²³ All measurements were performed with standard 100 μm triangular cantilevers (Digital Instruments) having a spring constant of $0.21 \pm 0.01 \text{ N m}^{-1}$. All measurements reported here were made using a scan size of $\pm 200 \text{ nm}$. A range of scanning frequencies were examined from 0.05 to 2 Hz. This equates to effective collision velocities between $2 \times 10^{-8} \text{ ms}^{-1}$ and $8 \times 10^{-7} \text{ ms}^{-1}$. As shown previously, these collision rates approximate well to those experienced by colloidal particles undergoing Brownian motion.^{24,25}

Table 1 Molecular weight analysis data for the polymer samples used in this study

Weight average molecular weight (M_w)	Number average molecular weight (M_n)	Polydispersity (M_w/M_n)
6780	6203	1.10
32 000	30 000	1.10
77 400	75 200	1.10
650 000	600 000	1.10

Results and discussion

Normalized force–distance data for the interaction of silica surfaces in solutions of sodium poly(styrene sulfonate) as a function of the polymer molecular weight are shown in Fig. 1 for a polymer concentration of 5000 ppm. Each data set shows a short-range monotonic repulsion close to the apparent zero separation distance. In the work reported here, there was never any evidence of a jump to contact that would indicate the presence of a primary minimum in this system. At larger surface separations, approximately 10–30 nm from the apparent zero separation distance, a secondary minimum in the data was seen for all polymers. The position and depth of this minimum is clearly influenced by the polymer molecular weight. As expected, the onset of the attractive secondary minimum is seen at larger apparent separation distances with increases in the molecular weight of the polymer sample.

Analysis of the force data in this paper is dependent upon our confidence in the measurement of the surface–surface separation distance. This is well known as a point of possible error since it depends on the establishment of a region of constant compliance where the two surfaces are intimately coupled and are moving as one. In the presence of surface adsorbed polymers, this can cause significant error in the separation distances.²⁵ In previous work, we have also shown how at large surface potentials and low electrolyte concentrations (*i.e.* Strong electrical double layer repulsions) an apparent constant compliance can be seen for weak cantilever springs that is many nanometres from true contact.²⁶ However, in this case we are using a relatively stiff cantilever spring and the concentration of polyelectrolyte is sufficient to ensure the surfaces can come into contact. Given this and the fact that we expect no surface adsorption of the polyelectrolytes, we are confident that the zero distance reported here is real and that all distances measured from it can also be taken as real.

The absence of a primary minimum in the measured force–distance data between the silica surfaces in aqueous electrolyte solutions, has been reported previously. The reasons

for this lack of a minimum in the data have not been conclusively proven but it is believed to be influenced by the presence of surface adsorbed and strongly hydrated silica polymers that can form a “hairy layer” at the surface of the silica.²⁷

Previous measurements of depletion forces in the presence of highly charged polyelectrolytes have reported on the presence of oscillations in the interaction force profiles caused by bulk structuring of the polymer chains.^{12,13} The length scales of these oscillations correlate well with the size of the depletant (colloid particles, micelles or polymer coils) and are attributed to long-range ordering normal to the solid/liquid interface. In the present investigation, oscillations in the data were rarely seen. In our previous work,²⁶ we have seen that the ability to measure these oscillations is dependent upon the radius of the probe and the cantilever spring constant; weaker springs than those used here are generally needed and a micron sized colloidal probe also aids the measurement of these oscillations. Note that primary focus of this paper is the ‘depletion’ interaction rather than the structural components at longer range and these were easily recorded here. It is also worth noting that by directly comparing TIRM data, which is extremely sensitive with excellent spatial accuracy, against colloid probe AFM force data it has been shown that there is some doubt in the position of any oscillations in the data but not in the position of the secondary depletion minimum close to the surface.²⁶ Hence, and on the basis of all these points we have sufficient confidence in the data presented here to allow quantitative comparison of both the force and distance measurements as a function of different polymer solution features.

An analysis of the influences of polymer molecular weight and concentration on the depletion interaction forces, for various monodisperse NaPSS solutions, has been previously reported.¹¹ Comparison of the data with scaling theory showed a good correlation between measured and predicted behaviour for these polyelectrolyte solutions. Of particular interest was the influence of polymer concentration on the depletion layer thickness (Δ). Plots of Δ versus polymer concentration were shown to follow a scaling law where $\zeta = kC^{-0.5}$. This is consistent with established theories for semi-dilute polyelectrolyte solutions where the scaling length is proportional to the Debye length (*i.e.*, $\kappa^{-1} \propto C^{-0.5}$). As a result of self-screening, the Debye length decreases with increasing polymer concentration.

A key feature to establish in any analysis of polymer depletion is the concentration regime (*i.e.* dilute or semi-dilute) in which the measurements are being made. The chain overlap concentration, C^* , may be calculated using $C^* = (16\pi l_B AL)^{-1}$, where l_B is the Bjerrum length, A is the linear charge spacing along the chains, and L is the contour length.²⁸ For the polyelectrolyte samples used here, C^* ranges from 1500 ppm for molecular weight 6780 to 28 ppm for molecular weight 650 K. Almost all of the data reported here, regardless of the molecular weight, are therefore recorded within the semi-dilute regime. It should be noted however that for the lower molecular weight samples the chosen solution concentration of 5000 ppm is close to the transition concentration.

Data for the depletion interaction measured in 3 different binary polymer mixtures are shown in Fig. 2–4. In each case,

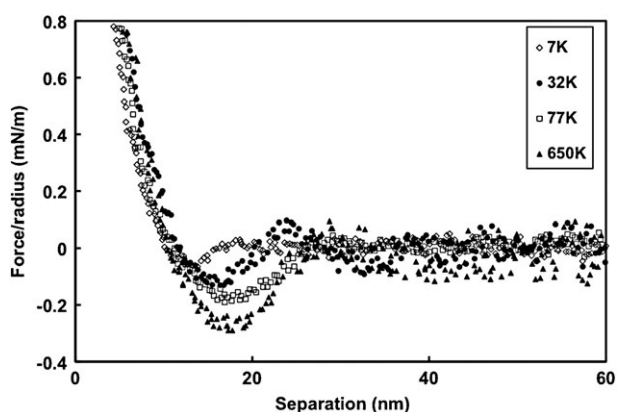


Fig. 1 Reduced force (F/R) as a function of separation distance for the interaction of a silicon cantilever tip (radius = 160 nm) with a flat silica substrate in salt-free NaPSS solutions at a bulk concentration of 5000 ppm. Data are shown for four different molecular weights, as indicated in the figure.

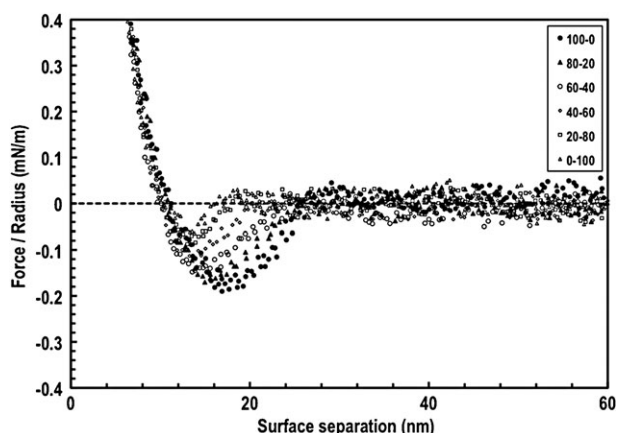


Fig. 2 Reduced force (F/R) as a function of separation distance for the interaction of a silicon cantilever tip (radius = 160 nm) with a flat silica substrate in binary mixtures of salt-free NaPSS solutions at a total bulk concentration of 5000 ppm. Data are shown for mixtures of the 77 and 7 kDa polymers; the compositions are as shown on the figure with the higher molecular weight component given first in each composition.

the data were collected at a fixed total polymer concentration of 5000 ppm. Before analyzing the detailed features of each data set, the general features should be noted. Clearly, in each case as the weight fraction of the binary polyelectrolyte mixtures is altered there is a systematic variation in the measured depletion interaction. Interestingly, there is a very clear variation in the position and depth of the minimum for both the 77 k/7 k mixtures and the 650 k/7 k mixtures but the 650 k/32 k system does not exhibit a clear change in the position of the minimum with changes in the composition.

Similarly to Fig. 1, each data set shows a monotonic repulsion at small separations. This repulsion is caused by the electrical double-layer repulsion between the charged silica surfaces inside the depletion layer. Exact analysis of this repulsion is difficult since the concentration of salt within the depletion layer will be influenced by the loss of polyelectrolyte

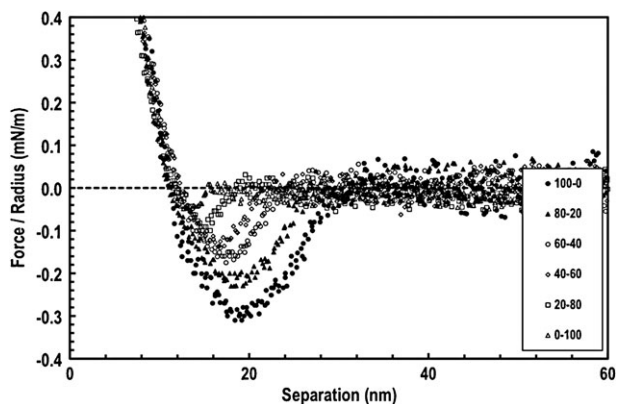


Fig. 3 Reduced force (F/R) as a function of separation distance for the interaction of a silicon cantilever tip (radius = 160 nm) with a flat silica substrate in binary mixtures of salt-free NaPSS solutions at a total bulk concentration of 5000 ppm. Data are shown for mixtures of the 650 and 7 kDa polymers; the compositions are as shown on the figure with the higher molecular weight component given first in each composition.

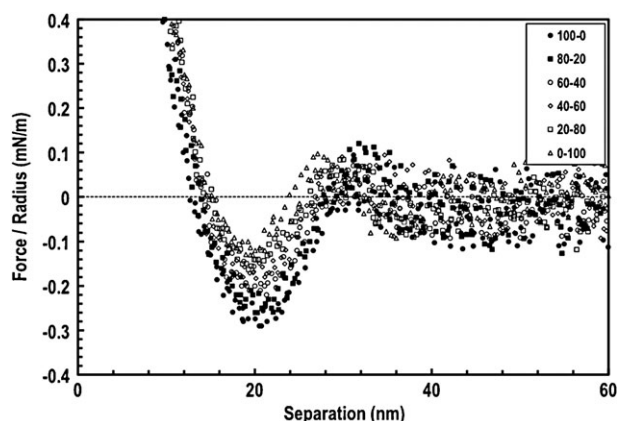


Fig. 4 Reduced force (F/R) as a function of separation distance for the interaction of a silicon cantilever tip (radius = 160 nm) with a flat silica substrate in binary mixtures of salt-free NaPSS solutions at a total bulk concentration of 5000 ppm. Data are shown for mixtures of the 650 and 32 kDa polymers; the compositions are as shown on the figure with the higher molecular weight component given first in each composition.

chains from this region. Furthermore, the presence of a depletion layer in an aqueous system will have an associated Donnan equilibrium that also causes a reduction in the interstitial salt concentrations. As a result, the Debye screening length will be influenced by the depletion effect and its quantitative prediction under these conditions is problematic.^{11,15}

Interestingly, for all the data shown here the measured Debye length was essentially fixed, as expected at a fixed polyelectrolyte concentration; since the electrolyte concentration will depend not on the molecular weight of the polymer but on the concentration of its constituent monomers and associated counter-ions. The strong correlation of the double-layer repulsion components in the total force curve is encouraging in terms of our confidence in comparing the position of the minima for different polyelectrolyte mixtures. We also note here, once again, that our earlier work comparing colloid probe data with that from TIRM measurements on an equivalent colloidal system to that used here gave definitive proof that the position of the secondary minimum is reliable; assuming certain other criteria are met, as discussed above.²⁶

The data presented in Fig. 1 to 4 can be considered to result from a linear summation of all the forces acting according to:¹⁵

$$F_{\text{total}} = F_{\text{vdW}} + F_{\text{edl}} + F_{\text{dep}} \quad (1)$$

where F_{vdW} is the attractive van der Waals component, F_{edl} is the repulsive electrical double layer force, and F_{dep} is the depletion interaction. Each of these components can be summarized as follows:

$$F_{\text{vdW}} = -\frac{AR}{6D^2}$$

$$F_{\text{edl}} = 8\pi\epsilon\psi_0^2 R^2 \left[\frac{\kappa}{(D+2R)} + \frac{1}{(D+2R)^2} \right] \exp(-\kappa D) \quad (2)$$

$$F_{\text{dep}} = \pi\Pi(D+2R)(D-2\Delta)$$

where A is the Hamaker constant, ε is the permittivity of the solution, D is the separation distance, and R is the probe radius. Following the previous approach,^{11,15} the fitting parameters are the surface potential (ψ_0), the Debye screening length (κ^{-1}), and the osmotic pressure of the polymer solution (Π). The depletion layer thickness (Δ) is obtained directly from the data and is assumed to be half the surface separation of the onset position for the secondary minimum as the two surfaces approach one another. The initial values of Π and ψ_0 were estimated from literature sources.¹¹ The best fits to the data were then obtained by iterative fitting of Π , ψ_0 , and $-\kappa^{-1}$. Values of the tip-surface potential ranged from -55 to -70 mV, and were seen to be invariant, within experimental error for any given probe tip.

The resultant best-fit parameters for the data shown in Fig. 1–4 are presented in Fig. 5–7. Looking first at the depletion layer thickness, Δ , as a function of composition (Fig. 5) we can see that in general there is an increase in the magnitude as the proportion of the larger molecular weight polymer sample increases for each of the three binary systems investigated here. It has been previously shown by many researchers that the magnitude of Δ is directly related to the polymer coil dimensions in solution and hence to the molecular weight. Previous reports for the same polyelectrolytes to those used here show good agreement with the magnitude of the Δ values reported. It is also clear from these data, as well as from Fig. 4, that the variation in Δ for the 650 k/32 k mixture is much less dramatic than we see for the other two samples that include the smallest polymer tested here with a molecular weight of 7 kDa. This relative insensitivity to composition change is further supported by the data for the osmotic pressure as a function of composition, Fig. 6.

It is interesting to speculate here as to why the systems including the lowest molecular weight polymer sample both show significant variations in Δ and Π as a function of composition whereas the system that includes two higher molecular weight materials is generally more insensitive. Jenkins and Vincent³ used self-consistent mean field calculations to show that for a binary mixture of monodisperse

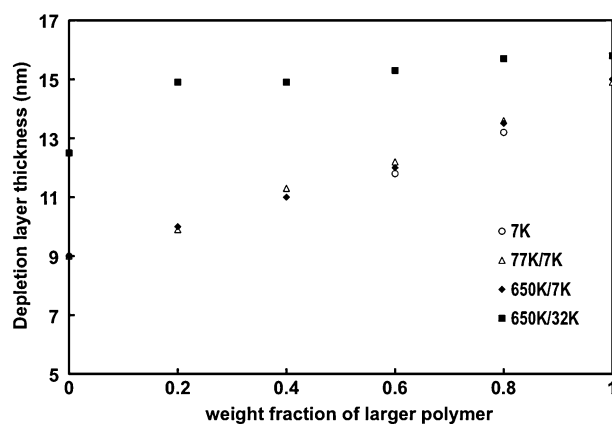


Fig. 5 The depletion layer thickness (Δ) as a function of the weight fraction of the larger polymer in the mixture for three mixtures of different molecular weights. Data for the homopolymer sample at 7 kDa is given for comparison at equivalent concentrations to those used here within the various mixture compositions.

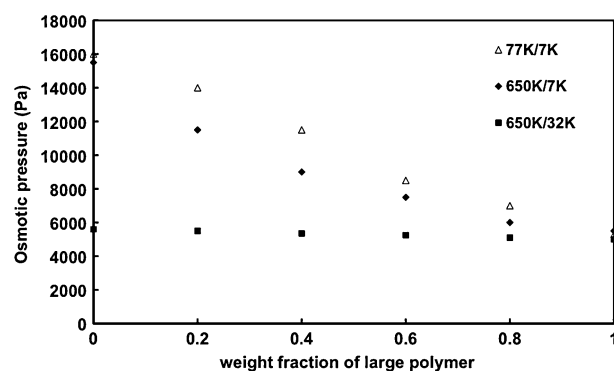


Fig. 6 The osmotic pressure (Π) as a function of the weight fraction of the larger polymer in the mixture for three mixtures of different molecular weights.

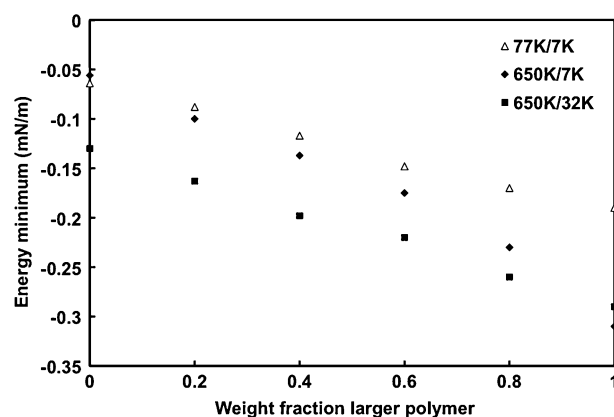


Fig. 7 The secondary energy minimum as a function of the weight fraction of the larger polymer in the mixture for three mixtures of different molecular weights.

homopolymers, we can expect the smaller molecular weight component to effectively control the overall depletion interaction. This is essentially because the depletion layer thickness is controlled by the smaller polymer, which resides within the depletion layer of the larger polymer component. However, it should be noted that when we are in a semi-dilute regime above the critical overlap concentration, C^* , the correlation length, ζ , which is essentially a measure of the distance between cross-over points (or entanglements) does not depend on the molecular weight but is instead dependent on the size of the monomer units and their overall concentration. In a previous paper,¹¹ data of the osmotic pressure (Π), for similar polymers to those used here, showed that at 5000 ppm and above Π was invariant for polymers with a molecular weight of 32 kDa and above. Some deviation in the value of Π was seen for the 32 kDa sample at the lowest concentration recorded of 1000 ppm. At all concentrations up to 10000 ppm, the lowest molecular weight sample (7 kDa) showed a larger value of Π at all concentrations. These observations are indicative of the low molecular weight sample being below C^* and the other polymers generally being above C^* . Looking once again at the data reported here, the lack of significant variations in Δ and Π for the 650 k/32 k binary mixture (Fig. 4) are consistent with both polymers being above C^* at

all concentrations; hence, a constant value of ζ should result in a constant Δ and Π should also be constant as predicted from theory. Broadly, this is what is seen here. In contrast, the two systems examined with the low molecular weight polymer (7 kDa) show strong evidence that this polymer sample is below C^* and is the primary determinant of the overall interaction forces through its presence inside the depletion layer of the larger molecular weight polymer. Assuming this is true, the strong variation in Δ and Π for these systems as a function of the binary mixture composition is consistent with our previous work which showed a strong variation in these values as a function of concentration for this polymer.¹¹

Conclusions

The forces of interaction between silica surfaces in solutions of binary mixtures of a non-adsorbing polyelectrolyte have been measured. The force–distance data were seen to have a secondary attractive minimum in all cases consistent with the presence of a depletion interaction. The position and depth of this minimum were seen to depend upon both the composition of the binary mixture and the molecular weights of the two polymers making up that mixture. Analysis of the data give direct proof that in binary mixtures, the low molecular weight component will be located within the depletion layer of the larger molecular weight component and can therefore control the overall interaction. This is consistent with previous theory predictions. The data further suggest that this finding is valid when the low molecular weight component only is below the chain overlap concentration, C^* . When both polymers are well above C^* , no clear differences are seen in the depth or position of the minima as a function of composition. This is also consistent with theory.

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