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Abstract
The formation of equilibrium clusters in colloidal particle suspensions, due to the balance of a short-range attraction and a long-range repulsion interaction, has been recently widely discussed, considering its important role in many areas of material science and soft-matter physics. In this work, we describe a simple phenomenological model in which particles interact with a screened electrostatic repulsive interaction modelled by a Yukawa potential and with a short-ranged attractive potential ('charge patch' attraction) due to the strong lateral correlations among the adsorbed polyions at the surface of the approaching particles. This 'correlated adsorption' generates a more or less ordered 'patchwork-like' surface structure with excess negative charge domains (adsorbed polyelectrolyte domains) and excess positive charge domains (polyelectrolyte free domains), which give rise to a short-range attractive potential. In low-density colloidal liposome suspensions, particles form stable equilibrium clusters. We investigated the cluster formation and the growth in the cluster size in cationic liposomal particle suspensions (built up by DOTAP and DOTAP/DOPE mixtures), by means of a dynamic light scattering technique, in several experimental conditions (adsorbing polyions of different molecular weights, liposomes of different surface charge densities, presence of added salt), and a generally good agreement with the model predictions has been found.

1. Introduction

Mixtures of anionic polyions and cationic liposomes self-assemble into various mesoscopic structures such as micelles, vesicles, lamellar and cubic phases, depending on a variety of different physico-chemical parameters. Among these meso-structures, there has been much

recent interest in studying polyion-induced particle aggregates and, in particular, their size evolution, induced under different modalities, because of their possible applications in drug delivery and in biomedical applications [1–3]. It is well known that addition of oppositely charged polyions to a suspension of colloidal charged particles promotes the growth of complexes that exhibit a spontaneous overcharging and a re-entrant condensation [4]. Both these two effects characterize a class of colloids, usually referred to as *attractive colloids*, that, besides their widespread use in biological and biophysical applications, represent valuable models for studying complex systems in the field of soft-matter physics.

Recently, the dynamic behaviour of short-ranged attractive colloids has been extensively investigated, both by theoretical [5, 6] and computational [7, 8] methods, and a rich and interesting phenomenology has been evidenced. Depending on the balance between attractive and repulsive interactions, under particular conditions, these systems show an equilibrium cluster phase, where particles form reversible, relatively large, aggregates.

A common way to realize, in a colloidal suspension, a short-range attraction contribution is obtained by the addition of *non-adsorbing* polymers which produce an unbalanced osmotic pressure in the depleted region, leading to an attractive effect by depletion interactions [9]. In this work, on the contrary, the aggregation of charged unilamellar vesicles (liposomes) is promoted by the addition of oppositely charged *adsorbing* polymers which form a strongly correlated liquid on the surface of liposomes, accompanied by a spontaneous 'overcharging' of the complexes, at the increasing polymer concentration. In this case, the short-range attraction, and hence the aggregation effect, is driven by the correlation energy gain at the place of contact when two approaching particles touch each other. This peculiar mechanism is responsible for the 'charge inversion' effect, which causes the 're-entrant' condensation and the formation of large, reversible aggregates, which occur only in a range of polymer concentration close to the neutrality condition of the complexes.

In this paper, we present a simple phenomenological model that provides evidence for the existence of an equilibrium cluster phase in low-density colloidal systems, governed by the competition of short-range attractive interactions and long-range repulsive interactions. This 'toy model' is able to describe the main features of the experimental findings and represents a useful tool for a better understanding of the observed phenomenology.

2. Experimental details

Unilamellar liposomes in aqueous solutions were obtained from cationic and neutral double-tailed lipids, dioleoyltrimethyl ammonium propane (DOTAP) and dioleoylethanolamine (DOPE). Materials were purchased from Avanti Polar Lipids (Alabaster, AL) and used without further purification. The liposome polyion coating and their aggregation have been induced by adding a highly charged linear polyion, polyacrylate sodium salt (NaPAA), that, thanks to its relatively simple chemical repeat unit, is a prototype of a polyion model. NaPAA samples were purchased from Polysciences (Warrington, PA) as 0.25 (wt/wt) aqueous solution, with nominal molecular weights 5, 60, and 225 kD, respectively. In all the experiments, the liposome concentration was maintained constant to the value of 1.5×10^{13} particle ml^{-1} and the mean hydrodynamic radius of the vesicles was about 40 nm with a log-normal size distribution with a polydispersity of the order of 0.20–0.25. The polyion–liposome complexes were induced by adding an appropriate amount of a polyion solution at the desired concentration to the liposome suspension in a single mixing step and gently shaking by hand.

The size characterization of the resulting complexes and the evaluation of their charge during the whole aggregation process was followed by means of dynamic light scattering and electrophoretic measurements.

2.1. Dynamic light scattering (DLS) measurements

The size and size distribution of the polyion-induced liposome aggregation has been measured by means of quasi-elastic light scattering technique, using an optical fibre probe (Brookhaven FOQELS) in conjunction with a Brookhaven 9000 AT logarithmic correlator, to compute the scattered light electric field time autocorrelation function. In the fibre-optic probe employed, a mono-mode optical fibre transmits a Gaussian laser beam to the scattering volume and a second one, positioned at a fixed angle of 137.5°, collects the scattered light. The main advantage of this apparatus is its larger insensitivity to multiple-scattering effects, when compared to more traditional DLS apparatus [10]. The relaxation times that characterize the diffusing movement of the liposome aggregates were found using the standard data analysis program CONTIN [11] in terms of a continuous distribution of exponential decay times. This analysis yields the average diffusion coefficient $\langle D \rangle$ which can be translated into the hydrodynamic radius R by the Stokes–Einstein relationship $R = k_B T / (6\pi\eta\langle D \rangle)$, where $k_B T$ is the thermal energy and η the viscosity of the solvent, respectively.

2.2. Electrophoretic measurements

The electrophoretic measurements were carried out by means of the laser Doppler electrophoresis technique using a MALVERN Zetamaster apparatus equipped with a 5 mW HeNe laser. The mobility u of the diffusing aggregates was converted into a ζ-potential using the Smoluchowski relation $\zeta = u\eta/\epsilon$, where ϵ is the permittivity of the solution.

3. Theory

The characteristic size of the clusters, upon polyion-coated liposome aggregation, is defined by the balance of a short range attraction and of a long-range electrostatic repulsion. The balance is attained when the last polyion-coated liposome (lipoplex) of average size R_0 sticks to a cluster of average size R already formed by $N \sim (R/R_0)^3$ identical lipoplexes. From now on, the equilibrium condition is reached and no other lipoplex can stick, since repulsion would overcome attractive interactions.

The electrostatic repulsion between particles of radii R_0 and R has, in units of $k_B T$, the Yukawa form [12], according to the DLVO theory [13]

$$U(r) = Z Z_0 l_B \frac{\exp(k_D R)}{1 + k_D R} \frac{\exp(k_D R_0)}{1 + k_D R_0} \frac{\exp(-k_D r)}{r} \tag{1}$$

where k_D^{-1} is the Debye screening length, l_B the Bjerrum length and r is the pair distance between particles and finally Z and Z_0 are the valences of the two approaching particles of radius R and R_0, respectively. As pointed out by Haro-Perez et al [12], although equation (1) has been derived in the Debye–Hückel approximation, in the case of highly interacting systems undergoing a charge re-normalization, its validity has been well assessed. Moreover, although the Yukawa potential was originally proposed as the screened potential between two identical charged spheres, its extension to different size aggregates has been recently discussed by Mossa et al [14], who demonstrated that the repulsion part of the resulting cluster–cluster potential is again of the Yukawa type.

The short-range attraction generated by adding adsorbing anionic polyelectrolytes to the liposome suspension has been modelled, for simplicity, with a constant term $\mathcal{E}$ which does not depend on the particle distance and is effective only when particles touch each other. Correlation between polyions adsorbed on the surface of a charged liposome leads to the effect of attraction, the aggregation being driven by the correlation energy gain at the place

of contact when two approaching particles touch each other [15]. The two potentials act at different length scales; the repulsion extends over a scale $k_D(R + R_0)$ larger than the scale length $R_G/(R + R_0)$, where R_G is the radius of gyration of the polyion in solution, typical of the attractive interaction. In the present case, for NaPAA of molecular weight 60 kD, R_G is of the order of 15 nm [16], corresponding to an attractive range of about 5–10% of R. This modelling of the inter-particle interaction potential is substantially equivalent to assuming an adhesive hard-sphere potential of Baxter [17], with a repulsive long-range tail modelled with the Yukawa term. Such a scheme to model attractive colloids has been used by several authors (see for example the recent work of Prinsen and Odijk [18]).

Since the polyion adsorption, at increasing polyelectrolyte/liposome ratio, produces the 'overcharging' effect, i.e. the charge of adsorbed polyelectrolytes exceeds the liposome charge and the overall charge of the polyion-coated liposome goes through zero and inverts the sign [19], the whole system shows a re-entrant condensation, with the size of the aggregates that shows a maximum when the whole aggregate is approximately neutral.

The balance condition, resulting in an aggregate of $(N+1)$ lipoplexes, is reached when the 'charge patch' short-range attraction $\mathcal{E}$ equals the electrostatic repulsion $U(r)$ at $r = (R + R_0)$, resulting in the relation

$$\frac{(1 + X)^3}{2 + X} = \frac{1}{\rho}(1 + b(1 + X))(1 + b) \qquad (2)$$

where $X = (R/R_0) - 1$, $b = k_D R_0$ and $\rho = (Z_{\text{eff}}^2 l_B/\mathcal{E} R_0)$. In the above expression, Z_{eff} is the valence of the polyion-coated liposome (of radius R_0) when the polyion adsorption has occurred. The valence of the polyion-coated liposome aggregate (of radius R) is approximated as $Z_{\text{eff}}(R/R_0)^3$. The balance condition (equation (2)) depends on two parameters, the dimensionless screening parameter b and the ratio ρ between the electrostatic repulsion energy $(Z_{\text{eff}}^2 l_B/R_0)$ and the typical attractive energy $\mathcal{E}$.

The Coulomb interactions between charged aggregates are screened by both free counterions and salt ions. The Debye screening length k_D^{-1} is determined by the number density of both counterions derived from polyion and liposome ionization (dissociation of their charged groups) and of positive and negative salt ions (in the presence of added salt, 1:1 simple electrolyte at a concentration C_s), according to the expression

$$k_D^{-2} = 4\pi l_B\left(\frac{C_{CL}}{2}g + fC_p + 2C_s\right) = 4\pi l_B \frac{C_{CL}}{2}g\left(1 + 2\frac{f}{g}\xi + \frac{4}{g}\frac{C_s}{C_{CL}}\right) \qquad (3)$$

where C_{CL} is the concentration of the charged lipid, C_p the concentration of the polyion and the parameters g and f take into account that a partial re-normalization of the charge is to be expected, due to the counterion condensation on both the polyion and on the charged liposome. The variable ξ defines the polymer to lipid molar ratio $\xi = C_p/C_{CL}$ (monomoles of polymer to moles of charged lipid). The concept of charge re-normalization in the electrostatic of highly charged colloidal suspensions has been discussed extensively in recent reviews [20, 21].

Figure 1 shows a typical behaviour of the normalized aggregate size (R/R_0) (equation (2)) as a function of both the polyion to lipid charge ratio ξ and the parameter a (see equation (6)) concerning the effective charge of the polyion-coated liposome derived from the electrophoretic measurements.

The effective charge of the polyion-coated liposome is a key parameter in determining the electrostatic interactions that govern the aggregation process. Generally speaking, the total number of ionizable groups on the liposome surface (the stoichiometric charge) can be calculated from the measured liposome radius and the area per charged head group, occupied by the different lipids at the liposome surface. This area can be estimated, for example, from
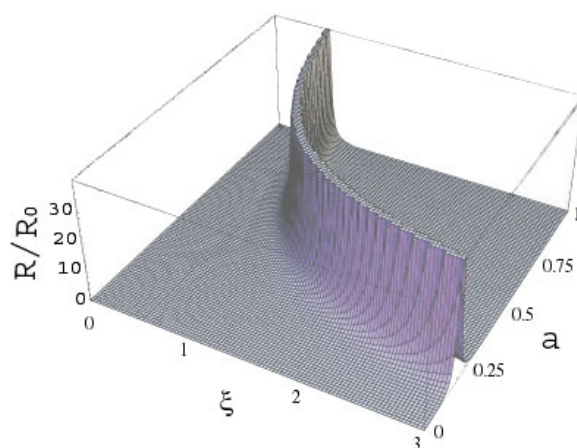
Figure 1. The dependence of the aggregate size R/R_0 on the polyion to liposome molar ratio ξ and on the parameter a (equation (6)).

(This figure is in colour only in the electronic version)

pressure–area isotherms of monolayers deposited at the air–water interface [22]. According to what is stated above, in the case of mixed liposome composed by cationic and neutral lipids, the effective surface charge on a polyion-coated liposome, taking into account the charge re-normalization effects through the parameters f and g, should be given by

$$Z_{\text{eff}} = 4\pi R_0^2 g \frac{(1 - \frac{2f}{g}\xi)}{A_{\text{CL}} + A_{\text{NL}} C_{\text{NL}}/C_{\text{CL}}} \tag{4}$$

where A_{CL}, C_{CL} and A_{NL}, C_{NL} are the area per head group and the concentration of the cationic and neutral lipids, respectively. However, this number usually does not coincide with the *effective* number of charges involved in inter-particle interactions. This is due to two concomitant effects, the incomplete group ionization at the effective conditions of the experiment and the screening effects of counterions.

In the case of pure DOTAP and DOTAP–DOPE (1/1 molar fraction), the effective ionization at the surface has been recently evaluated as a function of bulk pH by using a fluorescent, pH sensitive, probe, 4-heptadecyl-7-hydroxycoumarin [12]. Although these measurements suggested that DOTAP lipid is completely ionized at a bulk pH around 7.4, both in pure DOTAP liposomes and in the mixtures, nevertheless, for similar systems, it has been shown that the charge per particle obtainable from liquid-like structure factor, i.e. the effective charge which determines particle interaction, is significantly smaller than the stoichiometric charge [23]. Since the electrostatics of these systems dominates the interaction effects deeply, we have assumed that the 'electrokinetic charge' is a suitable parameter to quantify long-range repulsion interactions.

3.1. Determination of the effective particle charge (from ζ-potential measurements)

In this work, we have assumed that a reasonable estimate of the effective charge Z_{eff} of the lipoplexes can be evaluated from electrophoretic measurements, in the close proximity of the isoelectric condition, at the maximum of the aggregation size. To estimate this *effective charge*, we have measured both the radius R and the electrophoretic mobility u of the lipoplex aggregates that, at a fixed liposome concentration, form at increasing polyelectrolyte
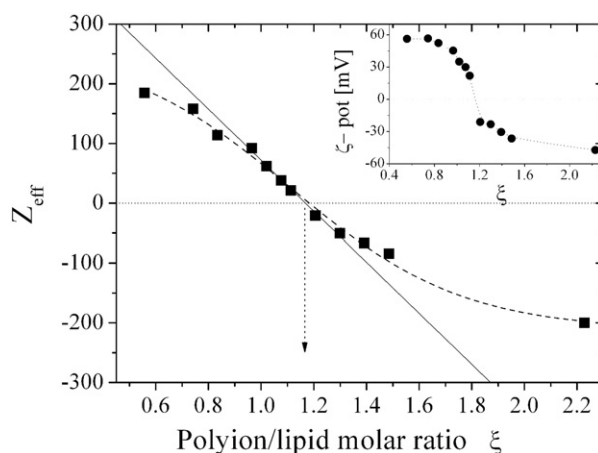
Figure 2. The effective charge Z_{eff} per polyion-coated liposome as a function of the polyion to lipid molar ratio ξ, derived from the electrophoretic measurements (equation (5)). Close to the isoelectric point, Z_{eff} varies linearly with ξ (full line). The inset shows the dependence of the measured ζ-potential of the liposome aggregate on the polyion to lipid molar ratio ξ.

content. By applying the O'Brien–White theory [24], ζ-potential has been obtained from the electrophoretic mobility and, from this quantity, the effective valence Z_ζ of the *whole aggregate* has been calculated by using the following expression:

$$Z_\zeta = \frac{4\pi\varepsilon_0\varepsilon_r k_B T k_D R^2}{e^2}\left[2\sinh\left(\frac{e\zeta}{2k_B T}\right) + \frac{4}{k_D R}\tanh\left(\frac{e\zeta}{2k_B T}\right)\right]. \tag{5}$$

The effective charge per polyion-coated liposome, Z_{eff}, is simply given by $Z_{eff} = Z_\zeta/(R/R_0)^3$.

As expected, due to the progressive neutralization of the liposome charge by the increasing number of the adsorbed polyion molecules, the effective charge Z_{eff} varies with ξ as shown in figure 2. Close to the isoelectric point, Z_{eff} decreases linearly as a function of ξ and this dependence can be approximated by a linear relationship

$$Z_{eff} = Z(1 - a\xi) \tag{6}$$

where the two parameters Z and a summarize, to a first approximation, both the polyion-coated liposome charge re-normalization and the counterion condensation on the polyion chain. The parameter Z has the meaning of an effective charge of the bare liposome. There is an obvious discrepancy between the values of Z obtained by fitting equation (6) to experimental data (figure 2), and the values of Z_{eff} in the limit of no added polyelectrolyte. However, this discrepancy is to be expected since the 'condensation effects' does not depend linearly on stoichiometric charge surface density [25]. Within this picture, factor a has the meaning of the fraction of effective charge on the polyion or, in other words, is the fraction of non-condensed, free counterions. The knowledge of the two quantities, Z and a, allows us to predict the aggregate size increase, close to the isoelectric condition, as a function of the added polyion.

4. Results and discussion

The above model has been applied to the polyion-induced liposome aggregation process in three different experimental conditions, i.e., by varying the molecular weight of the adsorbed polyion (we investigated aggregation in the presence of NaPAA of 5, 60 and 225 kD); by varying the surface charge density at the liposome surface (we investigated liposomes built up
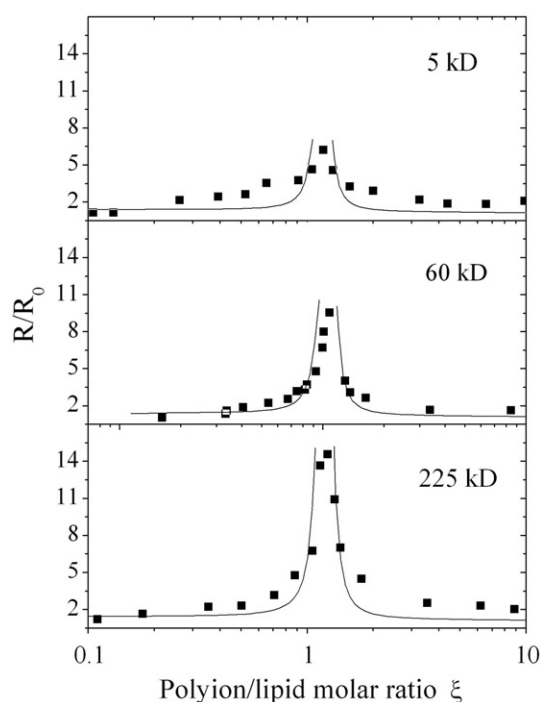
Figure 3. The normalized size R/R_0 of the polyion-coated liposome aggregates as a function of the polyion to lipid molar ratio ξ, for three different molecular weight polyions ($M_w = 5, 60$ and 225 kD). The full curves represent the calculated values according to equation (2), with a value of the attractive potential of $\mathcal{E}$ of 15, 25 and 40 (in units of $k_B T$). The values of the other two parameters (Z and a in equation (6)) are determined from the electrophoretic measurements (see the text for details). We obtain values of $Z = 630$ and $a = 0.93$, largely independent of the molecular weight.

by mixtures of DOTAP and DOPE, at different molar concentrations, between 1 and 0.35); and finally by adding to the aqueous phase a simple salt (NaCl) at an appropriate concentration, in order to vary the Debye screening length from about 8 nm (in the absence of added salt) to about 0.5 nm (in the presence of salt at 0.5 mol l^{-1}). Some typical results are summarized in figures 3 and 4, where the normalized ratio R/R_0 of the resulting aggregates is shown as a function of the polyion to lipid molar ratio ξ, during the whole aggregation process, below and above the isoelectric condition. As can be seen, a reasonably good agreement is obtained in all the systems investigated, even more if we consider that the aggregation is modelled on the basis of a single free parameter, the attractive energy $\mathcal{E}$. In the above analysis, the Debye screening length k_D^{-1} (equation (3)) has been evaluated, to a first approximation, neglecting the liposome charge re-normalization (g equal to unity and f derived from the value of the parameter a), and the other two parameters entering equation (2) are evaluated on the basis of the electrophoretic measurements and on the position of the maximum in the aggregate size, which corresponds to the isoelectric condition. These latter parameters are shown in figure 5, in the case of liposomes built up by mixtures of DOTAP and DOPE at different compositions. As far as the attractive interaction $\mathcal{E}$ is concerned, its strength is of the order of 25 $k_B T$ for a fully charged DOTAP liposome and progressively decreases as the liposome structural charge is reduced (mixed DOTAP/DOPE liposomes). For the other two systems investigated, we have found that $\mathcal{E}$ increases with the increase of the molecular weight of
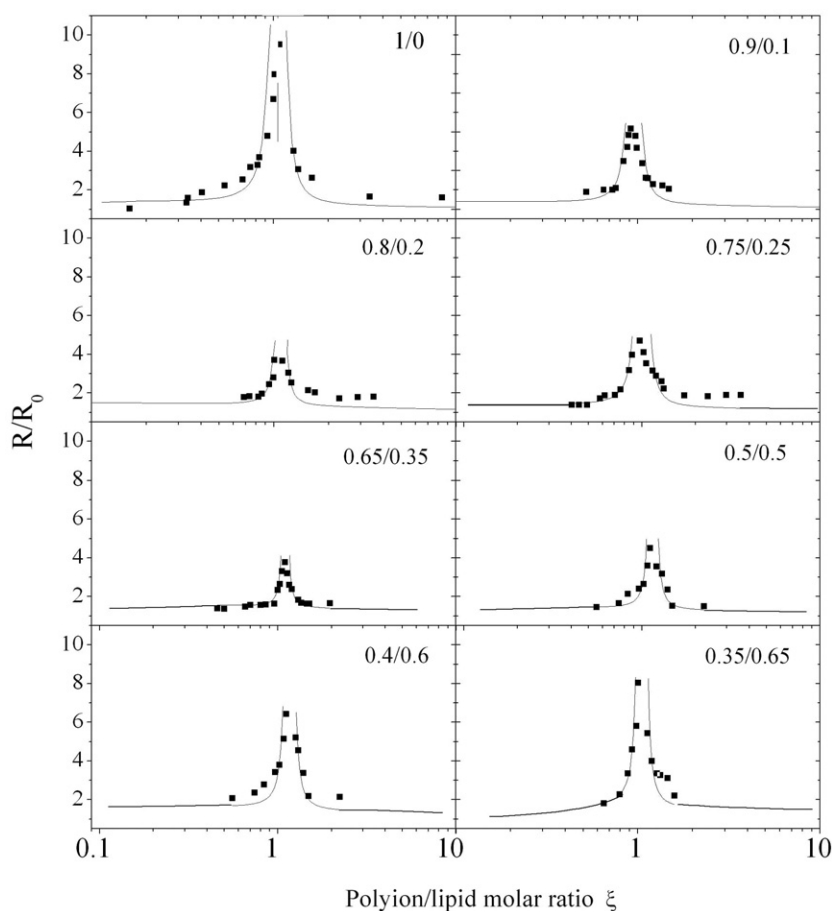
Figure 4. The normalized size R/R_0 of the polyion-coated liposome aggregates as a function of the polyion to lipid molar ratio ξ, for liposomes built up by DOTAP–DOPE mixture at different molar ratio. The polyion molecular weight is $M_w = 60$ kD. The lipid mixtures employed are indicated in each panel as DOTAP to DOPE molar ratio. The full curves represent the calculated values according to equation (2), with a single free parameter (the attractive potential $\mathcal{E}$). The values of the other two parameters (Z and a in equation (6)) are determined from the electrophoretic measurements (see the text for details).

NaPAA, from about 15 to 40 $k_B T$, as the molecular weight is increased from 5 to 225 kD and, analogously, $\mathcal{E}$ increases, approximately in the same range, with the increase of the salt concentration from 0.005 to 0.1 mol l^{-1} NaCl (inset in figure 5, bottom panel). The values of the energy $\mathcal{E}$ compare reasonably well with those estimated from the adhesion energy per unit surface for neutral vesicles (of the order of 0.3 mJ m^{-2} [26]), taking into account the adhesion surface area of the vesicle in the contact region and, moreover, that the adjacent surfaces are oppositely charged, with a relatively high charge density. It is worth noting that, despite the different physico-chemical conditions within which the liposome aggregation proceeds, this model is able to take into account the main phenomenology we have observed.

A final comment is in order. The parameter Z (figure 5) has the meaning of an *effective charge* of the bare liposome. There is a strong difference between the extrapolated values of Z_{eff} (obtained by the linear regression to experimental data close to the isoelectric point) and
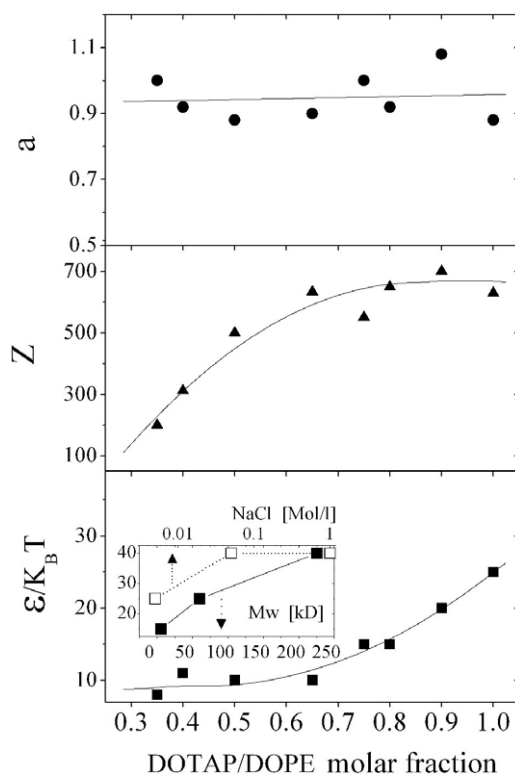
Figure 5. Dependence of the parameters a and Z describing the linear changes of the valence Z_{eff} close to the isoelectric point as a function of the liposome composition (liposomes built up by mixtures of charged (DOTAP) and neutral (DOPE) lipids). The molecular weight of the polyion is 60 kD. Bottom panel: the attractive potential $\mathcal{E}$ as a function of the DOTAP/DOPE molar ratio derived from the fitting procedure (equation (2)). The inset shows the value of $\mathcal{E}$ in the liposome aggregation induced by polyions of different molecular weights (5, 60 and 225 kD) and in the presence of added salt (NaCl, from 0.05 to 1 mol l^{-1}).

the values of Z_{eff} measured in the limit of no added polyion. Moreover, these quantities deeply differ from the value calculated on the basis of a full ionization and on the value of the area occupied by each head group at the liposome surface (equation (4)). However, this difference is to be expected since 'condensation effects', to which these differences are essentially due, do not depend linearly on the charge surface density [12, 27]. In particular, in the case of flexible polyions, a release of condensed counterions would require changes in the 'electrostatic blob' polyion conformation. A flexible, highly charged polyion can be represented as a chain of 'electrostatic blobs', with the statistics of the chain inside the blob determined by the thermodynamics of solvent–'uncharged chain' interactions [28]. The blob size results from a balance between the electrostatic energy of a blob and the polymer/solvent interfacial energy. Within this picture, since the electrostatic energy of a blob incorporates any effects of counterion condensation, a release of counterions affects the local chain conformation and has a cost in terms of chain entropy. Consequently, a significant increase of 'free counterions' should be expected only when electrostatic interactions become strong enough to deform the chain on length scales smaller than electrostatic blob size [29]. Practically, with the increase of the charge density on the surface, an increase of the fraction of 'free counterions' and, correspondingly, of the effective charge on the polyelectrolyte should be expected.

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