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# Complexing behaviors between ammonium polyacrylate and poly(diallyldimethylammonium chloride) polyelectrolytes

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## Abstract

The formation and complexing behaviors of non-soluble polyelectrolyte complexes (nPECs) between ammonium polyacrylate (A40) and poly(diallyldimethylammonium chloride) (PDC) polyelectrolytes at different A40/PDC mass ratios, pHs and $KNO_3$ concentrations were studied using particle size and zeta potential measurement techniques. It was found that the particle size distributions and surface charge behaviors of the formed nPECs were related to the mass ratio of participating polyelectrolytes and $KNO_3$ concentrations. Without addition of $KNO_3$, there was no nPECs formed at a mass ratio of 0.1. Both fine and large nPECs were formed at mass ratios of 0.2 and 0.6 while only fine nPECs formed at a mass ratio of 0.4. Increasing the mass ratio from 0.8 had no significant effect on particle size distribution. The observed complexing behaviors were related to the histories of charge neutralization degree of PDC and the surface zeta potentials of nPECs. The addition of electrolyte would result in bigger nPECs attributable to the shielding effect and weakened electrostatic interaction for polyelectrolytes and nPECs, and hence the linkage of nPEC became possible. The pH changes affected the surface zeta potentials of nPECs due to the variation in ionization of A40 molecules.

*Keywords:* Polyelectrolyte complexes; Particle size distribution; Surface zeta potential

## 1. Introduction

Interaction between oppositely charged polyelectrolytes in aqueous media leads to a new kind of polymeric compound, polyelectrolyte complexes (PEC). Both water-soluble and non-soluble complexes can be formed depending on many factors such as chain structure of participating polyions, pH, molar ratio, simple electrolyte concentration [1–5] and mixing condition [6]. Stoichiometric complexes will be formed between the strong polyions [7] while non-stoichiometric complexes will be formed between the strong polyions and weak polyions, or among weak polyions [2,8–10]. Polycomplexes formed by polyelectrolytes with a low charge density, so called coacervated complexes will separate from aqueous solutions in the form of a liquid concentrated phase. The studies devoted to coacervated complexes have been focused on the phase separation in mixture solutions of polyelectrolytes at various temperatures, pHs, polyelectrolyte and low-molecular-weight salt concentrations.

Previously, various experimental methods such as ultraviolet spectroscopy [11], light scattering [12–14], sedimentograms [15], viscometry [16,17], turbidimetry [18–21] and fluorescence spectroscopy [22–24] have been used to study the complexing behaviors of polyelectrolyte complexes in aqueous media. The objective of this work is to study the influences of mass ratio, pH and ionic strength on the complexing behaviors between the cationic polyelectrolyte poly(diallyldimethylammonium chloride) and the anionic ammonium polyacrylate. In this study, the particle size analysis technique and zeta potential measurement were used to characterize the formed nPEC particles,

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and they were proved to be the useful techniques for direct observation of different effects on the complex formation process.

## 2. Experimental materials and methods

### 2.1. Materials

The cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDC, molecular formula $(C_8H_{16}ClN)_n$, average $M_w$ 200,000–350,000, 20 wt% solution in water) was supplied by Aldrich Chemical Company, USA. The ammonium polyacrylate (A40, molecular formula $(C_3H_7O_2N)_n$ average $M_w$ 3500, 40 wt% solution in water) was supplied by Allied Colloids Co. Ltd, England. The molecular structures of PDC and A40 are shown in Fig. 1. The analytical grade sodium hydroxide, supplied by Aldrich Chemical Company, USA, was prepared into 0.1 and 1 M solutions using the deionized water. The deionized water was produced by using a Milli-Q reagent grade water system (Millopore GmbH, Eschborn, Germany).

### 2.2. Methods

The as-received PDC and A40 solutions were diluted to 1.5 mg/ml using the deionized water. Then, the $KNO_3$ was dissolved into the diluted solutions to obtain the PDC and A40 solutions containing 0, 0.02, 0.05, 0.1 and 0.2 M of $KNO_3$. The pHs of the diluted PDC and A40 solutions were about 6.8 and 7, respectively. The non-soluble polyelectrolyte complexes (nPECs) were prepared by adding the diluted PDC solution dropwise into a 200 ml glass beaker containing the diluted A40 solution with stir mixing (speed 200 rpm) until the predetermined A40/PDC mass ratio was achieved. The mixture solutions were further stirred for 1 h with pH monitoring and adjustment to the required values using the sodium hydroxide solution.

Three groups of nPEC suspension samples were produced according to the procedure described above. The first group of nPEC suspension samples formed without $KNO_3$ at various A40/PDC mass ratios was used to study the effects of A40/PDC mass ratio on the complexing behaviors through the measurements of particle size distributions, indexes of particle counts and surface zeta potentials at a defined pH of 7.5. The second group of nPEC suspension samples prepared without $KNO_3$ at different A40/MPDC mass ratios and various pH values was used to evaluate the effects of simple electrolyte $KNO_3$ and pH on the changes of particle surface charges. The third group of nPEC suspension samples prepared at an A40/PDC mass ratio of 1 and various $KNO_3$ concentrations was used to study the effects of $KNO_3$ concentrations and pH on the complexing behaviors. The zeta potentials of the nPECs were measured by using the Zetasizer4 (Malvern Instrument Ltd, England). The particle counts, $n$, were recorded during the measurement, which was then converted into the index of particle counts log $n$. The particle sizes of the nPECs were measured using a particle size analyzer (Mastersizer, Malvern Instrument Ltd, England). For each group of samples, the measurements were completed within 2 h after PEC preparation in order to avoid any possible errors due to the ageing effects, such as sedimentation and aggregation.

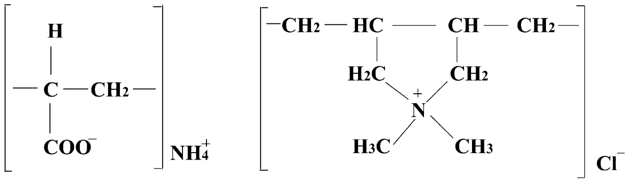

Fig. 1. The molecular structures of A40 and PDC.

## 3. Results and discussions

The polyelectrolytes can be classified into two types. They are the pendant type polyions with charges in the side groups and the integral type polyions with charges in the chain backbone. Both A40 and PDC are pendent polyions and their molecular structures are shown in Fig. 1. The PDC, because of the quaternary ammonium group, is a strong polycation, i.e. the dissociation degree of the ionic groups is independent of pH range [22]. Polyelectrolyte complexes are formed mainly by the strong electrostatic interaction between the oppositely charged macromolecules, but the hydrophobic interaction, van der Waals force and hydrogen bonding can also play the important roles [9,25]. The structures and compositions of the PECs obtained depend on the neutralization degree of the polyion, polymer structure, hydrophobicity, concentration of the complex, pH and ionic strength [2]. The driving force for the nPEC formation is the reduction of electrostatic repulsion force and increased hydrophobic force between the initially formed PECs due to charge neutralization. As a result, the PECs would be aggregated together to form the large nPEC particles. However, an nPEC particle may contain thousands of hundred of single PEC and thus, an nPEC particle could be seen as a macromolecule formed through the electrostatic and hydrophobic interactions. Therefore, any change in these two types of interactions would result in a structure change of the particles.

The theoretical stoichiometric point for the PEC formation between A40 and PDC was at a mass ratio of A40/PDC = 0.55 according to their molecular weights of the repeating units. The particle size distributions of the nPECs formed without $KNO_3$ at different A40/PDC mass ratios are shown in Fig. 2. The changes of surface zeta potentials and particle counts for the formed nPECs at different mass ratios are shown in Fig. 3. It was found that there was no nPEC formed at a mass ratio of 0.1. This could be attributed to the fact that when the A40/PDC mass ratio was 0.1, the A40

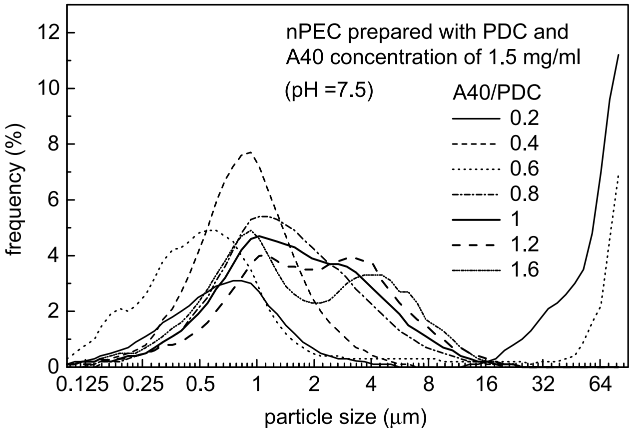

Fig. 2. The particle size distributions of nPECs formed at various A40/PDC mass ratios without $KNO_3$.

would neutralize only a small fraction of the charge sites on the PDC chains due to the small quantity of anionic polyelectrolyte A40 added into the system. The positive charges remaining on the PDC molecular chain were high enough to provide a repulsion force to prevent the adhesion and coiling of the water-soluble complexes (sPECs) chains through hydrophobic force.

When the A40/PDC mass ratio was increased to 0.2, the positive charge on the PDC chain would be further neutralized and hence the hydrophobic force overcame the electrostatic repulsion force among the initially formed sPECs. Consequently the sPECs would coil together to form the particles with a very dense core part (dark area) and less dense outer layer (gray area). The density of the particles would decrease from the particle center to outer layer due to gradually decreased charge neutralization of PDC with the process of adding A40 into the system. The schematic representations of the formed sPECs and nPECs are shown in Fig. 4. The formation of large nPECs at a mass ratio of 0.2 might be interpreted by introducing a bridging concept. This suggestion was based on the fact that theoretically it is not possible to get a homogeneous mixture between A40 and PDC and equal charge neutralization degree for all PDC and A40 molecules before the nPECs were formed. Some of the positively charged nPECs could be linked by A40 bridges to form very loose nPECs and therefore, less particle count was observed as shown in Fig. 3. However, when the mass ratio was 0.4, the formed nPECs particles were very fine with narrow particle size distribution from 0.15 to 4 μm. At the same time, the quantity of the formed particles was also significantly increased. This is because the charges on the PDC chains were significantly neutralized at such a mass ratio closing to the stoichiometric point of 0.55. Therefore, the significant reduction in electrostatic repulsion force between the initially formed sPECs would allow the formation of small dense particles with higher density.

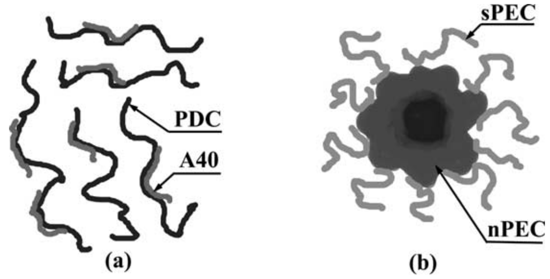

Fig. 4. Postulated structures of the formed sPECs (a) and nPECs (b).

There were both very fine and big nPEC particles produced simultaneously and the particle counts was the highest when the mass ratio was 0.6. At this ratio, slightly over the theoretical stoichiometric point, the neutralization degrees of both participant polyelectrolytes were high, and hence a very dense complex structure (fine nPECs) was expected to form [26]. At the same time, the linkage of small nPECs by PDC leading to the formation of large nPECs also happened. This explanation was supported by the fact that the surface zeta potentials of the nPECs were changed from positive to negative due to the excess of A40 as clearly demonstrated in Fig. 3. The slightly higher particle count was attributed to the formation of extremely fine particles

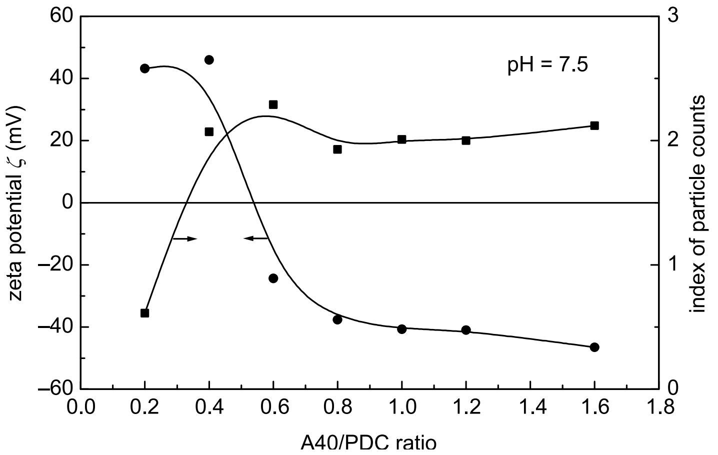

Fig. 3. The changes of zeta potentials and indexes of particle counts for the nPECs formed at different A40/PDC mass ratios without $KNO_3$.

for the same cause at a mass ratio of 0.4. Further increase of A40/PDC mass ratio over 0.8 had no significant effect on the distributions of nPEC particle sizes, as well as the zeta potentials. This could be interpreted by the reason that the nPEC surface was already negatively charged at a mass ratio over 0.8 and therefore, further linkage of small highly negatively charged nPECs to form larger particles would be prohibited.

The zeta potential measurement of the formed nPECs revealed many important features of the formed PECs. An interesting behavior of the nPECs formed at A40/PDC mass ratios of 0.2 and 0.4 was that the zeta potentials of the nPECs was nearly the same and decreased sharply at a mass ratio higher than 0.4, as shown in Fig. 3. This phenomenon was also reported by Kramer et al. [10], but they did not explain it. As discussed above, there was charge neutralization difference occurred during the formation of nPECs. When the mass ratio was below 0.4, the A40 molecules reacted with some of the PDC molecules to achieve a nearly maximum interaction. This would lead to the formation of dense particles with a high charge neutralisation degree. However, some PDC molecules were neutralized at a lower degree and would absorb onto the nPECs surfaces. As a result, the surface charges reflected only those of the PDC on particle surface, regardless of the A40/PDC mass ratio. From Fig. 3, it can be seen that the formed particles carried zero charge on their surfaces at a mass ratio of about 0.6 that agreed well with theoretical calculation. This may indicate two important features; (1) the induced ionization of A40 was quite high, (2) the diluted solution could give a relatively homogeneous interaction for polyelectrolytes. It was also noticed from this measurement that the surface charge behaviors of the formed particles were limitedly affected by the mass ratios relatively far away from the theoretical stoichiometric point, for example below 0.4 or over 0.8. This result suggested that the surface charge behaviors were mainly determined by sPECs on the surface of nPEC that could carry either positive or negative charges depending on the mass ratio. From this study, it could be predicted that theoretically it is not possible to form the nPECs with zero surface charge or 100% stoichiometric nPECs even between strong polyions.

In order to exam the effect of pH on the surface charge behaviors of the nPECs, the zeta potential measurement was carried out at different pH values and the results are shown in Fig. 5. When the mass ratios were 0.2 and 0.4, the charges of nPECs were nearly constant until pH 8, then decreased slightly with further increase of pH. The same phenomenon has also been reported by Xia et al. [27] for protein–polyelectrolyte complexes. This result suggested that the A40 on the surfaces of the nPECs had not been fully ionized by complexing when the mass ratio was below 0.4 even at a pH of 8. Therefore, the A40 molecules on the surfaces of the nPECs would be further ionized at a higher alkali media. As a result, the negative charges on the nPECs surfaces would increase and the zeta potentials decrease. When the mass ratio was over 0.6, some PDC molecules would be first neutralized by A40 to form the nPEC core part. The induced ionization of A40 still reached nearly maximum in this core part, then other PDC molecules were further neutralized by A40 with a lesser degree of induced ionization to form the outer part of nPEC particles. At the outermost part of the particles the sPECs with less A40 ionization simply attached onto the formed particles. The A40 molecules attached on the outside of the nPECs did not have the same ionization degree as inside. The ionization degree of A40 on the surfaces of nPECs decreased with increasing mass ratio. The ionization degree of these A40 molecules would be increased with increasing pH. This was reflected by the decrease of surface charges with pH for the nPECs formed at mass ratios of 0.6, 0.8 and 1 as shown in Fig. 5. The changes of the zeta potentials shown in Fig. 5 were attributed to the result of adsorbed A40 molecules on the outer layer of the particles whose ionization degree increased with pH.

Complexing behavior could also be affected by the simple electrolyte in solution. Fig. 6 shows the changes of zeta potentials and particle counts of the nPEC suspensions formed at an A40/PDC mass ratio of 1:1 with different

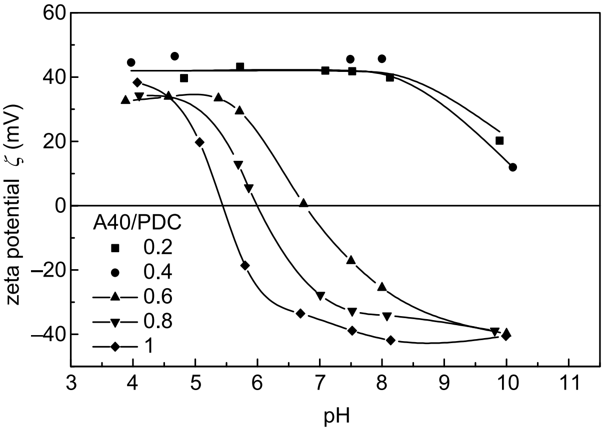

Fig. 5. The changes of zeta potentials with pH for the nPECs formed at different A40/PDC mass ratios without $KNO_3$.

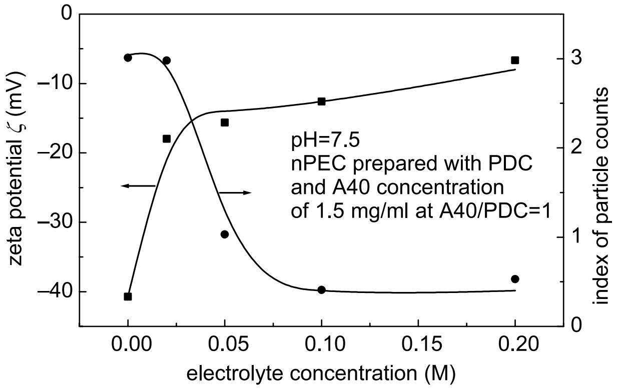

Fig. 6. The changes of zeta potentials and indexes of particle counts of the nPECs formed at A40/PDC = 1 with different $KNO_3$ concentrations.

$KNO_3$ concentrations. It can be clearly seen from this figure that the addition of 0.02 M $KNO_3$ had no effect on particle counts but caused a significant increase on surface zeta potential. With further increase of $KNO_3$ concentration, the surface zeta potentials and particle counts increased and decreased slightly, respectively. The particle size analyses of the nPECs shown in Fig. 7 indicated there were both fine and large nPECs formed from about 0.25 to 8 μm when there was no electrolyte added. However, very large nPECs particles with size from about 1 to 30 μm started to form when the $KNO_3$ concentration was 0.02 M. The particle size distributions were similar for the nPECs formed at $KNO_3$ concentrations of 0.05, 0.1 and 0.2 M. But a small amount of very large particles with size over 30 μm were formed at a $KNO_3$ concentration of 0.2 M.

The significant increase of zeta potentials with addition of 0.02 M $KNO_3$ could be attributed to the weakened electrostatic interaction between the polyelectrolytes by small electrolyte ions [28]. As discussed earlier, the nPECs were formed mainly through electrostatic interactions. Small electrolyte ions reduced the Coulombic force between the positive and negative charges by shielding [29]. This would result in a reduction of the induced ionization of A40 by complexing and therefore, the total number of negative charges provided by A40 molecules were decreased as reflected by significant increase of zeta potentials and nPECs particle size. With further increase of $KNO_3$ concentration from 0.05 M, the shielding effect became more significant leading to even weaker electrostatic interaction between A40 and PDC molecules. This would result in considerable decrease on induced ionization of A40 molecules and increase of zeta potential. Hence, the electrostatic repulsion force between the nPECs became weaker and there would be more chances for the initially formed nPECs to link together forming large nPECs. The result was less particle counts. At the same time, the density of the formed particles became lower due to weakened attraction force. This complexing behavior has also been suggested by Tsuchid et al. [2] and Ström et al. [30]. They claimed that a complex coacervate, a liquid containing large amount of water, will be formed at a high electrolyte concentration. The present studies support the theory that there would be no compact PEC structure formed at a threshold electrolyte concentration.

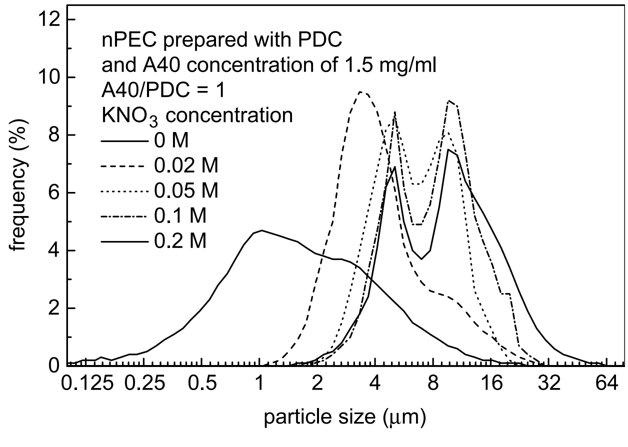

Fig. 7. The changes of particle size distributions of the nPECs formed at A40/PDC = 1 with different $KNO_3$ concentrations.

## 4. Conclusions

It was found from this study that the formation mechanism of the nPECs could be well elucidated through the investigations of particle size and surface zeta potential. Both mass ratio and electrolyte concentration had significant influences on the particle size and surface charging states of nPECs. Without electrolyte addition, the formation of both fine and large particles at mass ratios of 0.2 and 0.6 was attributed to the linkage of nPECs by A40 at a mass ratio of 0.2 and the linkage of nPECs by PDC and the nPEC aggregation due to reduction of surface zeta potentials at a mass ratio of 0.6. Very fine particles were formed at a mass ratio of 0.4 where both the charge neutralization of PDC and surface zeta potential were relatively high, thus prevented the linkage and aggregation of nPECs. There was no significant change in particle size distribution when the mass ratio was higher than 0.8. The study also revealed that when the mass ratios were far away from the theoretical stoichiometric point, the zeta potentials were not affected very much by the mass ratio because only those A40 or PDC on the particle surfaces dominated their changes. The behavior of surface zeta potential change with pH for the nPECs was attributed to the ionization changes of A40 molecules. The addition of electrolyte would result in bigger nPECs attributable to the shielding effect and weakened electrostatic interaction and hence the linkage of nPEC became possible.

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