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Supplementary Information: Counterion Condensation on Spheres in the Low-salt Limitt

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1 Synthetic details

1.1 Materials

Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($Na^+[TFPhB]^-$) was donated by Merck Chemicals Ltd UK. and used without further purification. A comb copolymer composed of poly(12-hydroxystearic acid) chains grafted to a poly(methyl methacrylate-*co*-glycidyl methacrylate) backbone was used to sterically stabilise the particles, and was supplied as a solution in mixed acetates and precipitated by dropping into excess ice-cold methanol, dried in vacuo and redissolved in dried dodecane before use. Methyl methacrylate (MMA) was purchased from Sigma Aldrich and purified with a inhibitor removal column to remove the monomethyl ether hydroquinone (MEHQ) inhibitor. All other reagents used were purchased from Aldrich, or Acros Organics and used without further purification. Dodecane and hexane were dried with the aid of activated 4 Å molecular sieves.

1.2 Synthesis of ionic monomer [IM2][TFPhB]

The charged colloids were prepared by doping poly(methyl methacrylate) (PMMA) latex particles with a polymerisable ionic monomer (IM) composed of one of the cations **1-4** and anion **5**, shown in Fig. 2 of the main text. The synthesis follows the procedures detailed in our earlier work[1]. So, for example, n-tridodecyl-propyl-3-methacryloyloxy ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [IM2][TFPhB] was synthesised as follows. Tridodecylamine was reacted with 3-bromo-1-propanol to produce the quaternary ammonium salt n-tridodecyl-propyl-hydroxy ammonium bromide. After purification this was reacted with methacryloyl choride in the presence of triethylamine as a catalyst to yield n-tridodecyl-propyl-3-methacryloyloxy ammonium bromide. Finally an ion exchange was performed in ice-cold methanol with Na[TFPhB] to yield the final polymerisable ionic liquid n-tridodecyl-propyl-3-methacryloyloxy ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ([IM2][TFPhB]) as a viscous yellow liquid.

1.3 Synthesis of polymer particles containing IM2

In a typical preparation methyl methacrylate (MMA), methacrylic acid (MAA) and ionic monomer [IM2][TFPhB] were weighed into a three-necked round bottom flask along with hexane, dodecane, 2,2'-azobis(isobutyronitrile) (AIBN) initiator, together with a dodecane solution of the comb copolymer stabiliser and 1-octanethiol. The masses of each component are listed in Table 1.

Table 1 Dispersion polymerisation of batch **L7**

Component	Weight / g
MMA	2.2
MAA	0.05
([IM2][TFPhB])	0.2817
Stabiliser solution[a]	2.42
AIBN	0.04
Dodecane	1.5
Hexane	2.42
1-octanethiol	0.025

[a] As 30% wt solution in dodecane

The round bottom flask was equipped with a condenser, septum and magnetic stirrer bar. The reaction mixture was purged with nitrogen for 15 minutes before being lowered into a stirred oil bath which had been preheated to 80°C. After 10 minutes the reaction mixture turned opalescent, indicating that nucleation had occurred. After 2 hours, diethanolamine and an amount of dodecane equal in mass to the amount of hexane used initially were added and the temperature raised to 120°C. After 18 hours the flask was removed from the oil bath and the dispersion was filtered through glass wool in order to remove large aggregates. The flask was then rinsed with approximately 80 ml of dry dodecane.

References

1 G. Hussain, A. Robinson and P. Bartlett, *Langmuir*, 2013, **29**, 4204–4213.