Charge inversion and colloidal stability of carbon black in battery electrolyte solutions

Yan Zhang, Aditya Narayanan, Frieder Mugele, Martien A Cohen Stuart and Michel H.G. Duits

Physics of Complex Fluids Group, University of Twente and MESA+ Institute

PO Box 217, 7500 AE Enschede, the Netherlands.

Abstract

We studied the influence of salt on a commercially available carbon black (Ketjenblack 600, KB) in carbonate solvents commonly applied in rechargeable batteries. Adopting the typically used salts: lithium hexa-fluorophosphate (LiPF_6), lithium bis(trifluoromethane sulfonyl) imide (LiTFSI), as well as sodium hexafluorophosphate (NaPF_6) dissolved in mixtures of ethylene carbonate and propylene carbonate, we investigated both the zeta potential and the flocculation kinetics of the KB particles as a function of salt concentration between 0.01 mM and 1.0 M. Clear evidence was found for the preferential adsorption of cations. In the absence of salt, KB was found to carry a negative surface charge, but this gets neutralized by Li^+ at very low concentrations (~ 1 mM), and by Na^+ at intermediate concentrations (~ 30 mM). In the case of lithium ions, the increased adsorption at higher concentration led to a recovery of the colloidal stability around 3 - 30 mM, depending on the anion. At high concentrations exceeding 30-100 mM, all salts cause flocculation of the KB particles, due to a reduction of the electric double layer thickness. Since the charge neutralization of the KB by Na^+ takes place in the same concentration regime, no re-entrant stability is found for Na^+ . These findings could have implications in formulation protocols for semi-solid flow batteries, or other systems where an intermediate stable regime could assist mixing and/or structure formation at small length scales.

Keywords: semi solid flow batteries, carbon black, zeta potential, flocculation, stability ratio, re-entrant stability

1. INTRODUCTION

The development of sustainable energy storage systems has become an urgent issue due to the limited amount of fossil fuels / natural gas and their huge rate of consumption. Rechargeable lithium ion batteries are one of the most developed in the past few decades and commonly applied in portable electronics, electric vehicles, aerospace devices, etc. [1]. Flow batteries offer more flexibility than solid form batteries,

but the energy density of flow batteries is relatively low [2]. A new type, the so-called semi-solid flow battery (SSFB), was invented by MIT and has both the advantage of flow battery's flexibility and the high energy density found in solid batteries [3]. SSFBs differ from other batteries in that their electrodes are dispersions or suspensions, often composed of conductive nanoparticles (CNPs, often carbon black) and electrochemically active particles (EAPs, normally metal oxides which accommodate or release lithium ions during charge and discharge) in electrolyte solutions. Electrons reacting at the redox active particles are conducted by the CNPs to and from current collectors connected to an external circuit.

Since the emergence of SSFBs in 2011, optimization of their composition (EAPs, CNPs, solvent, salt) has been explored [4, 5] by measuring the rheological, electrochemical and conductive properties of the fluid electrode in order to understand and improve battery performance. Here colloidal interactions play a crucial role, via their determining influence on both the structure and the dynamics of the fluid. The CNPs, in spite of being present at much lower volume fractions than the EAPs, often dominate both the conductive and rheological behavior of the entire fluid via the formation of a flocculated network. Besides that, the colloidal interactions between active and conductive particles can influence the battery performance [6, 7]. However, the situation at present is that only little is known (and much is left to optimize) about the structure and strength of the (EAP surrounded) CNP network, an important reason being that the colloidal interactions between the CNPs are yet to be fully understood.

Both the specific solvent and the used salts (the electrolyte solutions) in SSFBs are the reason for this lack of knowledge. Similar to classical lithium batteries, the electrolytes in SSFBs are typically solutions of Li or Na salts dissolved in carbonate solvents. For example, $\text{Li}(\text{Na})\text{PF}_6$, $\text{Li}(\text{Na})\text{TFSI}$, $\text{Li}(\text{Na})\text{BF}_4$, $\text{Li}(\text{Na})\text{ClO}_4$ are used as salts, while ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) are used as solvents. Various combinations of these salts and solvents result in different electrochemical properties [8-10].

In more common solvents such as water, ethanol, hydrocarbons, etc., the behavior of Carbon Black has been better studied. Since van der Waals attractions between CBs are ubiquitous, surface oxidation followed by surface modification generally has to be applied in order to disperse carbon black [11-13]. In aqueous systems, the surface charge likely originates from carboxylate groups, while the extent of screening can be controlled via the salt concentrations. In non-polar solvents there is little screening of the electrostatic interactions, while the surface potential can vary per system (the origin is not always clear). In the battery community, the mixture of EC and PC is recognized as one of the best performing solvents [8, 14]. Both EC and PC cannot be ranked amongst conventional solvents, since they are aprotic while having a high dielectric constant. The latter allows dissociation of certain salts up to high concentrations (as needed for achieving high conductivity). In turn, the dissociated ions can change both the surface

potential and the electric double layer thickness. This could mean that the electrostatic interactions bear similarity to those in aqueous systems. However, even in that case there might be practical differences in the behavior at low salt concentrations, because the sensitivity of carbonate solvents to impurities is quite high.

A particular process that could modify the electrostatic particle interactions, is specific ion adsorption. Depending on the signs of the native surface charge and the adsorbing ion, even reversal of the surface charge is possible. This phenomenon has been studied for a variety of colloids [15-20] , including many oxides in aqueous environments [15-17]. Sign reversal of the zeta potential induced by alkali metal cations such as Li^+ and Na^+ has been found in a few cases (e.g. [21]), while for protons it is a well-known phenomenon, also in non-aqueous solvents [15].

In this paper we focus on the principal aspects of the colloidal stability of Carbon Black suspensions in electrolyte solutions containing the same ingredients as in a typical SSFB. We chose three electrolyte solutions, namely LiTFSI, LiPF_6 and NaPF_6 dissolved in a 1:1 binary mixture of EC and PC. Measurements of the zeta potential as a function of salt concentration are combined with determinations of the time-dependent average hydrodynamic (aggregate) diameter with Dynamic Light Scattering (DLS). By starting the DLS experiments with the suspensions in a non-flocculated state, we measure the flocculation rate, and calculate the stability ratio. Combining the observations from the two types of experiments allows us to draw conclusions about the ion adsorption and stabilization mechanism.

2. THEORY

In this section we summarize the approach and key equations as used to measure the stability ratio of the KB particles, as a function of salt concentration. The initial stage of the flocculation of particles with uniform size and shape can be described via the second-order reaction:

$$\frac{dN}{dt} = -kN^2 \quad (1)$$

where N is the concentration of the non-flocculated particles and k is the flocculation rate constant. Early stages of the flocculation process can be analyzed by measuring the average hydrodynamic radius (R_h)

with DLS as a function of time [22]. The linear dependence of R_h on time in this regime allows to

determine $\frac{dR_h}{dt}$, which is proportional to the flocculation rate. The average hydrodynamic radius is

calculated using the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi\eta R_h} \quad (2)$$

Where D is the measured diffusion coefficient, η the viscosity of the medium and k_B the Boltzmann constant and T the absolute temperature. Unlike many aqueous salt solutions, the viscosity of solutions in carbonate solvent depends significantly on the salt concentration: it nearly triples when the concentration of LiTFSI [23], LiPF₆ [24] and NaPF₆ [25] reaches 1 M (see also Appendix). This is of importance when calculating R_h , but also for the proper normalization of the flocculation rate: in more viscous media, the diffusion-limited flocculation of particles takes longer. This aspect, expressed by the factor $K_{Smol} = \frac{8k_B T}{3\eta}$ in the Smoluchowski equation is taken into account by multiplying η_r and dR_h/dt , where ($\eta_r = \eta_{sa}/\eta_{so}$ with η_{sa} the viscosity of the salt solution and η_{so} likewise for the solvent). The stability ratio [26, 27] is then defined as:

$$W = \frac{[d(R_h \times \eta_r)/dt]_{max}}{d(R_h \times \eta_r)/dt} \quad (3)$$

This quantity equals 1 (regardless of the viscosity) in all cases of unhindered flocculation. Repulsive interactions give rise to an energy barrier, which slows down the flocculation and hence increases W . In the limit where the particles do not flocculate at all, W approaches infinity.

We remark that the use of $\frac{dR_h}{dt}$ to calculate the stability ratio relies on the assumption that R_h increases linearly with time, which can only be expected in the early stages of the flocculation [28]. This implies that the analysis should be performed well within the so-called half-time, in which the number of entities is reduced by a factor of two:

$$t_{1/2} = 3\eta/4k_B T N_0 \quad (4)$$

3. EXPERIMENTS

3.1. Materials and sample preparation

Carbon black (Ketjenblack 600JDP) (KB) was obtained from AkzoNobel (the Netherlands) and dried in a vacuum oven for 24 hours before use. Ethylene carbonate (EC) (anhydrous 99%+ purity, <0.005% water) and propylene carbonate (PC) (anhydrous 99.7%+ purity, <0.002% water) were obtained from Sigma Aldrich (the Netherlands) and used as received. The binary mixture of EC and PC was 1:1 by volume (henceforth referred to as EC PC 1:1). LiTFSI (99% purity) was obtained as a gift from Solvionic (France). LiPF₆ and NaPF₆ (99%+ purity) were both purchased from Alfa Aesar (the Netherlands). All salts were used as received. Samples for SEM imaging were prepared by spreading a paste-like mixture of KB in ethanol on cleaned silicon wafers followed by drying in ambient air for half an hour.

KB stock suspensions (0.01%wt) were prepared by mixing the powder with EC PC 1:1 in an MBraun Argon-filled glove box (O₂, H₂O < 0.5 ppm), followed by ultrasonic treatment for 15 minutes. Samples for DLS and zeta potential measurements were prepared by initially mixing the required amount of the stock dispersion with EC PC 1:1 in polystyrene cuvettes; they were then removed from the glove box and sonicated for 15 minutes. Finally, salt solution (the concentration varied from 1.5×10⁻⁴ M to 1.5 M) was added. The mixtures were then allowed to equilibrate for at least 24 hours and sonicated for another 15 minutes before the experiments. DLS and zeta potential measurements could only be performed outside the glovebox.

3.2. Measurement of hydrodynamic radius and zeta potential

Hydrodynamic radii of the KB aggregates were measured as a function of time in a Malvern Nano ZS zetasizer using sealed polystyrene containers. Immediately prior to each experiment, the sample was sonicated for 5 minutes to obtain a well-defined, non flocculated starting state. Considering that the start-up time of the DLS measurement amounts ≈2 minutes, and that about 30 minutes are needed for a reliable measurement of $\frac{dR_h}{dt}$, we have aimed $t_{1/2}$ to be ≈ 1 hour. According to Eq. 4, N_0 should then be ≈ 3×10¹⁴ particles/m³. Since our unit particles are sintered (i.e. permanent) aggregates with complicated fractal-like shapes (see below), the quantitative relation between the theoretical N_0 and the experimental weight fraction w is not known. In the expression:

$$w = \frac{N_0 v_p \rho_p}{\rho_s} \quad (5)$$

with v_p the solid volume of a unit particle, and ρ_p , ρ_s the mass densities of KB and solvent (respectively ≈1.8 and 1.25 g/mL), v_p is unknown. Measurement of the hydrodynamic radius with DLS gave $R_h \approx 350$

nm. Assuming that the contour of the fractal-like particle is a sphere with this radius, and estimating the internal filling volume fraction to be ≈ 0.06 , we obtain $w=1.3 \times 10^{-6}$. Using this mass fraction in the preparation of the suspensions, we obtained a good linearity in the data of R_h vs time (see Fig. 4).

Zeta potentials were measured in the same zetasizer using a solvent-resistant dip cell. Samples were transferred into the cell inside the glovebox, sealed during transportation to the Zetasizer, and measured under Nitrogen protection. A thermal equilibration time of 120 s at 25 °C was allowed before starting the measurements. The measurement voltage was always in the range of 4.5 to 20 V. The instrument calculates the electrophoretic mobility U_E from the average particle velocity and the electric field strength, where the latter is calculated from the measured ion current and the conductivity of the continuous phase. The zeta potential ξ is then calculated from the electrophoretic mobility, using an appropriate model. We take the simplest equation from Smoluchowski:

$$U_E = \frac{\varepsilon \xi}{\eta} \quad (6)$$

with ε the dielectric constant of the continuous phase [29], for which we have taken that of the solvent.

Considering the aforementioned complicated particle shape, we refrain from taking electrophoretic retardation and relaxation corrections into account; values reported here are therefore to be considered as estimates rather than precise determinations.

4. RESULTS AND DISCUSSION

4.1. KB in pure EC PC solvent

Carbon black contains 90-99% carbon; this makes it strongly hydrophobic [30] and hardly dispersible in water. Generally, CB in suspension exist as units of chemically connected nanoparticles. Particle sizes have been reported to be 794 nm when suspended in water, and 181 nm in ethanol, in both cases much larger than the size of subunits that can be distinguished in electron micrographs [31]. Surface modifications such as oxidation introduce carboxylic groups and significantly improve the colloidal stability in both aqueous and non-aqueous solvents [32]. The adsorption of surfactants such as poly (oxometalate) is also effective to disperse carbon black in water, as aggregates smaller than 100 nm [33].

Some key properties of the Ketjenblack particles used in our experiments are summarized in Table 1, and are further discussed below. SEM images of (Figure 1) show structural subunits with diameters of around 20-30 nm. In contrast, the hydrodynamic radius R_h as measured by DLS was 350 ± 88 nm. This clearly indicates that in EC PC 1:1 (without added salt), KB exists as structures that are much larger than the 20-

30 nm units. To examine the nature of connections between the small building blocks, we subjected the suspensions to dilution (down to the detection limit of the DLS) and ultrasonication (for at least 1 hour). In either experiment, no significant changes in R_h were observed. Additional tests in which the particles were left to settle due to gravity (a behaviour that was manifested in the flocculated systems) did not shown any signs of sedimentation, even after several days.

Each of these observations indicates that KB is colloidally stable in EC PC 1:1 (without added salt). The zeta potential of KB, measured to be -47 mV, shows that the particles carry a significant negative surface charge, which is likely responsible for the colloidal stability. The fact that the overall hydrodynamic radius is much larger than that of the 20-30 nm structures indicates that the latter are chemically bound (rather than flocculated). No further effort was taken to disperse KB into smaller sizes; the fractal-like 350-nm particles were treated as permanent and inseparable in this particular solvent.

Figure 1. SEM image of Ketjenblack.

Table 1. Particle radius (from SEM and DLS) and zeta potential of KB in EC PC 1:1 in absence of salt.

	R_{SEM} (nm)	R_h (nm)	Zeta potential (mV)
KB	~15	350 ± 88	-47

The origin of surface charge for particles suspended in a liquid can be protonation or deprotonation of functional surface groups (typically hydroxyl) [34], adsorption of ions from solution [35], solvation and release of the ions from the particle [16], or a combination of these [36, 37]. Which mechanism(s) is(are) applicable depends on the particle surface chemistry, whether the solvent is protic or aprotic, the dielectric permittivity of the solvent (affecting the solvation of ions), etc. In case of particles in non-aqueous solvents with a low dielectric constant, it is generally less clear where the surface charge comes from. Impurity ions and moisture could play a role [38]. For carbon blacks, the origin of the surface

charge is even more complex, due to its source or batch dependent surface chemistry. For example, carbon atoms may bond with hydrogen and oxygen containing groups, such as quinone, ether, aldehyde and phenol, which act as defects. The zeta potential of carbon nanotubes depends on the dielectric constant of the dispersing medium, and varies in both value and sign because electron transfer occurs at different defect sites [39]; this may apply to CB as well. Furthermore, Kosmulski [21] and Xu *et al* [31] ascribed the surface charge and potential in non-aqueous solvents to an electron transfer between the particles and the solvent.

Specific for our system is that EC and PC have high dielectric constant (EC: 90; PC: 64) which could allow protons of the carboxylic groups on the CB surface to dissociate. [12]. It is also possible for the oxygen lone pairs in EC and PC to transfer to the carbon black surface. We speculate that the negative surface charge of KB in EC:PC comes from a combination of these two mechanisms.

4.2. KB in electrolyte solutions

4.2.1. Ion dissociation

Anticipating that the colloidal stability of KB will be intimately related to the presence of ions, we first examine the relation between the amount of dissolved (1:1) salt per unit volume (c), and the actual free ion concentrations. There are two extreme regimes where these two quantities may differ significantly. At the high concentrations corresponding to SSFBs, the salts may not be completely dissociated anymore, while at very low concentrations, (trace) impurities from the materials themselves or from the environment may significantly contribute to ionic composition of the liquid.

Measurements of the electric conductivity provide a suitable way to examine both regimes. They were performed with the Zetasizer as part of the determination of the zeta potential of the KB particles. To assess whether in these measurements also the KB could contribute to the conductivity, we compared the conductivities the salt-free solvent with and without KB. Both were measured to be 1.7 ± 0.1 $\mu\text{S}/\text{cm}$, indicating that the contribution of KB is indeed negligible.

Equivalent conductivities

Figure 2 shows for each of the three salts, how the apparent molar conductivities (conductivity due to added salt, divided by the concentration) depend on the salt concentration. For concentrations roughly between 0.1 and 100 mM, the (normalized) conductivities are constant per salt, indicating that the salts are completely dissociated, and contributions of other components than the salt alone, are negligible.

Figure 2. Apparent molar conductivity of LiTFSI, LiPF₆ and NaPF₆ versus concentration of salt. The background conductivity of the solvent was subtracted; For $c < 0.1$ mM, large error bars result after the subtraction and normalization. For $c=0.01$ mM some data points are shifted horizontally to allow distinction between different experiments.

In the low salt concentration regime below 0.2 mM, the apparent molar conductivities fall slightly above the values expected for the amount of dissolved salt. This could mean that (for the PF₆ salts) some additional ions were via impurities. Assuming a specific conductivity comparable to HCl, Kortschot et al [40, 41], found impurity concentrations of around 0.02 mM.

Water, as present in the starting materials, or as taken up from the ambient atmosphere might be a source of impurities. According to manufacturer, the water content of a EC-PC mixture should be $< \approx 35$ ppm, while other investigators have measured it to be < 20 ppm [42]. Moisture in the system could change the surface potential of particles dispersed in nonaqueous systems [21]. Furthermore, LiPF₆ and NaPF₆ are known to react with water to produce HF and F⁻ [43, 44] while LiTFSI is rather stable. The relatively high equivalent conductivity of Li(Na)PF₆ at < 0.1 mM salt compared with that of LiTFSI might thus be attributed to water. However, experiments aimed at corroborating this hypothesis by adding water, turned out inconclusive.

We now turn to the regime of high salt concentrations. Both EC and PC have a high dielectric constant, which favours ionization. However for $c > 10$ mM, it is indicated from the conductivities that ion pair formation becomes significant. In literature, the degree of dissociation (α) has been estimated to be 0.67

for 0.6 M LiTFSI [45], 0.67 for 1.0 M LiPF₆ [46] and 0.34 for 0.7 M NaPF₆ [25] in EC PC 1:1. Inserting these numbers into the expression for the dissociation constant (K):

$$K = \frac{\alpha^2 c}{1-\alpha} \quad (7)$$

and calculating the actual ion concentrations as a function of the concentration of added salt, we find that the dissociation is almost complete below 10 mM for each of the salts, while for higher concentrations the degree of dissociation (at the same c) follows the order: NaPF₆ < LiTFSI < LiPF₆. We remark that the equivalent conductivities in Fig. 2 do not follow this trend; suggesting that in EC:PC the mobility of Na⁺ is higher than that of Li⁺.

Debye lengths

From the measurements in Fig. 2 and the assumed specific conductivities, the Debye length κ^{-1} can be calculated. In the calculations we included the both the added ions and impurities in the solvent. The concentration of the latter was estimated from a comparison with the conductivity of pure solvent, similar to [40, 41]). Possible ion concentration changes due to the reaction with moisture were not taken into consideration. In Figure 3 we plot it against $\frac{1}{\sqrt{c}}$ for the three electrolyte solutions.

Figure 3. Debye length against the inverse of the square root of the salt concentration for LiTFSI, LiPF₆ and NaPF₆. Solid lines are drawn to guide the eye. Inset shows the same data in a log-log plot.

In case of complete dissociation and absence of impurities, this plot should show a straight line with a slope of $\sim 10 \text{ mM}^{0.5} \text{ nm}$. This appears to be the case for concentrations in the range 0.25 – 5 mM. At lower concentrations (higher $c^{-1/2}$), the effects of the impurities show up, while at higher concentrations the effect of incomplete dissociation becomes visible as an upward curvature (see the log-log plot in the inset).

Clearly, the thickness of the electric double layer undergoes strong variations as the salt concentration is varied between 10 μM and 1 M, reaching the nm range (where van der Waals interactions play a role) at concentrations around 0.1 M (similar to aqueous systems). A calculation of κa (assuming the aggregate radius to be relevant) reveals that $\kappa a \gg 1$ (i.e. relatively thin double layers) for all salt concentrations investigated. This justifies the calculation of zeta potentials using the Smoluchowski equation (as was done in Sec. 2). Another observation from Fig. 3 is that the variations in Debye length between the different salts at the same concentration, are generally minor; suggesting that any differences in colloidal stability of KB in presence of the different salts are not be related to differences in screening.

4.2.2. Zeta potential and colloidal stability of KB

Figure 4 shows some typical curves of the time-dependent hydrodynamic radius of KB particles in solutions of EC PC 1:1 containing different amounts of salt (in this case LiTFSI). In this graph R_h is multiplied with the relative viscosity of the salt solution (compared to salt-free solvent), to allow direct comparison of the slopes representing the flocculation rates (see Sec. 2). The concentration-dependent viscosities of the different salt solutions are given in the Appendix.

The R_h values themselves are all close to 350 nm at the beginning of the experiment; this confirms that all experiments were started with non-flocculated particles. Table 2 lists the numerical data for all flocculation experiments with LiTFSI, together with estimated errors.

Figure 4. Hydrodynamic radii multiplied by the relative viscosity for KB as a function of time at different concentrations of LiTFSI. The lines are the linear fits.

Table 2. Flocculation rate of Ketjenblack in LiTFSI solutions with different concentrations.

Concentration of LiTFSI (mM)	Viscosity (mPa.s)	Normalized flocculation rate (nm/min)	Stability
0.16	2.32	0.58±0.20	Stable
1	2.32	6.29±0.21	Unstable
2	2.33	7.85±0.30	Unstable
4	2.33	6.95±0.14	Unstable
8	2.35	6.92±0.20	Unstable
16	2.38	1.03±0.28	Unstable
64	2.53	0.22±0.28	Stable
128	2.75	0.81±0.19	Stable
256	3.21	1.36±0.51	Unstable
512	4.21	6.01±0.57	Unstable
1000	7.33	6.89±0.84	Unstable

It can be concluded from Fig. 4 and Table 2 that different regions of colloidal stability of KB are found on varying the concentration of the LiTFSI salt. At very low salt concentration (≤ 0.1 mM) the size of the KB particles remained constant, indicating that the suspensions were colloiddally stable. Between 0.1 and 10 mM LiTFSI flocculation occurred, corresponding to a first critical flocculation concentration (CFC). However on the addition of more salt, colloidal stability was recovered, as evidenced by a constant R_h at concentrations between 10 and 100 mM. Visual observation of samples in this regime did not show any significant sedimentation, even after weeks, thus confirming colloidal stability.

To allow a closer inspection and enable a mechanistic explanation, we now consider the stability ratio in conjunction with zeta potential. Figure 5a shows these data for KB in solutions of LiTFSI. A very large change in zeta potential is observed, from -47 mV in absence of salt (not shown) to $+28$ mV at 10 mM LiTFSI. Inversion of the sign of the zeta potential takes place between 1 and 10 mM, while the loss of colloidal stability occurs between 0.1 and 1 mM, where the zeta potential is already close to zero (-15 mV). These observations appear to be consistent with each other. The change in zeta potential is clearly caused by (preferred) adsorption of cations, in this case (predominantly) Li^+ . Increasing the salt concentration beyond 10 mM causes the zeta potential to gradually decrease again, leading to a second loss of colloidal stability and hence a second CFC at around 100 mM. The zeta potential is found to be (now $+$) 15 mV in this regime. The reason for the second flocculation is the strong electrostatic screening;

the Debye length is only ≈ 1 nm (see inset of Fig. 3). A CFC of around 100 mM is a typical value for solvents of high dielectric constant; many aqueous systems have similar CFCs for monovalent salts.

It is interesting to compare the findings for LiTFSI with those for LiPF₆. If the adsorption of cations is the main reason for charge inversion and re-entrant colloidal stability, similar findings are expected for the two salts. Fig. 5b suggests that this is indeed the case. However the salt concentrations where the transitions occur, appear to be somewhat smaller for LiPF₆. Additionally, at the same salt concentration, the zeta potentials of KB were higher in the case of LiPF₆ as compared to LiTFSI. Both differences might be due to the creation of protons, through the reaction of PF₆ anions with trace water. Due to their small size, protons can be expected to adsorb relatively easily as compared to larger ions. Moisture has also been reported to cause charge reversal of silica particles in non-aqueous suspensions [47].

Interestingly, a similar sign reversal of zeta potential from negative to positive as that reported in Fig. 5 was induced by alkali metal cations in other nonaqueous solvents like alcohols and dioxane for silica, titania, and other materials [17]. Remarkably, the sign reversal was observed at relatively low concentrations of cesium and potassium, while lithium and sodium salts were less efficient. Recent papers [48, 49] have addressed intercalation of several alkali metals into carbon via DFT calculations.

The measurements on NaPF₆ solutions allow another comparison with the case of LiPF₆. The data shown Figure 5c indicate that remarkable differences exist. Although charge (and zeta potential) inversion also occurs with NaPF₆, a significantly larger amount of salt is needed, suggesting that the tendency for Na⁺ to adsorb onto KB, is weaker. Additionally the finding that the zeta potentials are generally lower for the NaPF₆ case is consistent. The reason for this weaker adsorption may be attributed to the much larger ion radius of Na⁺ (0.19 nm) as compared to Li⁺ (0.07 nm). Remarkably, the re-entrant colloidal stability found for LiPF₆ is not observed with NaPF₆. As the charge inversion for NaPF₆ occurs at much higher salt concentration, screening due to the additional salt prevents re-stabilization in this regime.

As a final comment we briefly report a series of zeta potential measurements with NaPF₆, in which less strict precautions were taken, i.e. using the dip cell in open air (rather than an atmosphere of nitrogen). In this case, where the samples become more easily contaminated, the zeta potential was found to be more or less stable at -10 mV for NaPF₆ concentrations below 1 mM. This less negative potential (as compared to -20 to -30 mV in Fig. 5c) could suggest that proton adsorption play a role. The fact that now only ~ 1 mM NaPF₆ was needed to achieve charge inversion, would be consistent with that.

Figure 5. Stability ratio (open blue circles) and zeta potential (filled black squares) of KB as a function of (a, top) LiTFSI, (b, middle) LiPF₆ and (c, bottom) NaPF₆ concentration. Solid lines are drawn to guide the eye.

5. CONCLUSIONS

Carbon black particles carry negative a surface charge and form colloidally stable suspensions in the binary solvent of ethylene carbonate and propylene carbonate. The addition of salt neutralizes the negative surface charge and causes flocculation of particles, followed by charge inversion at higher salt concentrations, due to the further adsorption of cations (lithium or sodium ions). For some systems this gives rise to a re-entrant stability at salt concentrations around 10 mM. The salt concentration where charge inversion occurs is around 1 mM for both LiPF₆ and LiTFSI although there are minor differences due to specific cation-anion interactions. Sodium ions show a much lower adsorption affinity to our carbon black, causing the NaPF₆ concentration needed for charge inversion to be much higher (10-100 mM). Related to the stronger electrostatic screening, a re-entrant stability is not found for the sodium salt. Similar patterns of re-entrant stability occur in aqueous systems containing specifically adsorbed (cat)ions.

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APPENDIX

Table A1. Concentration dependence of the viscosity of the 3 salt solutions. Literature values for the viscosities of LiTFSI [23] and LiPF₆ [24], and measured values for NaPF₆ were fitted with second order polynomials, with concentrations expressed in mM and viscosities in mPa.s. The mean relative error indicates the quality of the fit.

Salt	Offset (m.Pas)	Linear term	Quadratic term	Mean relative viscosity error
LiTFSI	2.39	0.0022	$2.56 \cdot 10^{-6}$	2%
LiPF ₆	2.30	0.0015	$3.53 \cdot 10^{-6}$	8%
NaPF ₆	2.33	0.0017	$1.48 \cdot 10^{-6}$	4%

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