

Electro-hydrodynamic generation of monodisperse nanoparticles in the sub-10 nm size range from strongly electrolytic salt solutions: governing parameters of scaling laws

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Abstract A charge reduced electro-hydrodynamic atomization (EHDA) device has been used to generate airborne salt clusters in the sub 10 nm size range. The focus of this study on that specific sub-micron range of electrospray droplets with relatively high electrical conductivities and permittivities aims to address the still existing controversy on the scaling laws of electrosprayed droplet diameters. In this study different concentrations of sodium chloride and potassium chloride—both show strong electrolytic behavior—have been electrosprayed from solutions in pure water, or from aqueous ammonium acetate buffer liquids of varying concentrations. The dry residue salt cluster diameter generated by the EHDA process have been measured using a differential mobility analyzer. The initial droplet diameter has been determined indirectly

from the measured particle size following the steps of Chen et al. (J Aerosol Sci 26:963–977, 1995). Results have been compared to existing scaling laws valid for direct droplet measurements. They can be interpreted concisely on the basis of a realistic hypothesis on possible electrochemical effects taking place and affecting the droplet and thus nanoparticle formation in EHDA. The hypothesis developed in this work and the comparison with the experimental results are shown and discussed in the manuscript.

Keywords EHDA · Scaling laws · Electrolytes

Introduction

Recently the electrospray method for the generation of very small particles experienced a rapid development. This technique also known as electro-hydrodynamic atomization (EHDA) has been already described in the beginning of the 20th century (Zeleny 1917). The atomization process is based on the fact that conductive liquids pushed through a thin capillary may form conically shaped menisci as a result of electrostatic forces and surface tension when an electrical field is applied upon it. Depending on the electrical field strength the electrospray can be operated in different modes, described in great detail by Cloupeau and Prunet-Foch (1989, 1990) or discussed also in more recent works (Jaworek and Sobczyk 2008). In the

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present study only the cone-jet operating mode has been used and thus only this mode will be further discussed. In the cone-jet operating mode a cone (Taylor cone) is formed at the capillary tip (Taylor 1964). A thin jet emerges at the tip of the cone and subsequently breaks into fine, homogenous, and highly charged droplets in an arbitrary charge state. Exposing such airborne droplets to a bipolar cloud of atmospheric ions results in a well-defined (in terms of charge level) aerosol (Liu and Pui 1974).

This led to the development of charge reduced EHDA where the initially highly charged droplets produced at the capillary tip of the electrospray device are exposed to a high concentration ion cloud generated by either radioactive radiation or corona discharge for charge reduction before liquid evaporation. This way the mass to charge ratio can be kept below the Rayleigh limit and avoids Coulombic explosions of the droplets (Chen et al. 1995; Cloupeau 1994; Scalf et al. 1999). Charge reduced EHDA has opened the road for the aerosol generation of nearly arbitrarily small particles as demonstrated for sucrose particles as small as 4 nm (Chen et al. 1995), or proteins (Bacher et al. 2001).

This study focuses on the governing parameters of scaling the final size of the salt clusters based on the EHDA generation of salt particles in the range from 2 to 10 nm in terms of electrical mobility diameter measured with a differential mobility analyzer (DMA) (Winklmayr et al. 1991). Two salts with similar properties in terms of solubility in water and structure [sodium chloride (NaCl) and potassium chloride (KCl)] have been used to determine the impact of different concentrations in liquid solutions on the resulting generated particle size distributions. From the measured particle size distribution, following the steps of prior studies, we reconstruct the possible originally electrosprayed droplet size. The results have been compared with previously published scaling laws (Fernandez de la Mora and Loscertales 1994; Gañán-Calvo 1997a, b). Considering that aqueous solutions of NaCl and KCl are strong electrolytic liquids with a high electrical permittivity whose salt concentration strongly affects their conductivity, one may expect a significant deviation of the scaling law governing the particle size from that applicable to the originally electrosprayed droplets. Thus, the particular measures and considerations to calculate the original droplet size are crucial in this study.

The motivation for this work was to investigate electrosprayed droplets in the sub-micron size. This droplet size range very often entails the use of relatively conductive polar liquids (relatively high electrical conductivities and permittivities), a parameter range still claimed as a realm where the droplet diameter D_d may scale with the liquid flow rate Q as $D_d \sim Q^{1/3}$ (Fernandez de la Mora and Loscertales 1994; Chen et al. 1995). In contrast, the scaling laws introduced by Gañán-Calvo (1997a, 1998) claim that the liquid polarity does not influence D_d for any value of the electrical permittivity as far as the liquid is electrosprayed in cone-jet mode. In this case, the droplet diameter should scale as $D_d \sim Q^{1/2}$. The latter scaling law was successfully compared to a large series of direct droplet size measurements taken from an ample existing literature (Gañán-Calvo and Montanero 2009). Given the existing controversy, in this work the experimentally measured particle sizes have been carefully processed to calculate the original droplet size following different alternative hypotheses:

1. The droplet chemical composition simply mirrors the original liquid composition, as in previous works e.g., Lenggono et al. (2000) or Basak et al. (2007).
2. The electrochemical process of electroosmotic ion migration in the cone-jet under the strong applied electric field produces a fundamental mass (ions) imbalance in the chemical composition of the solute in the electrosprayed droplet. This ion imbalance can be calculated with sufficient accuracy on the basis of charge and mass conservation using existing, well-established scaling laws for the issued electric current.

Both experimental collections of calculated droplet sizes are compared to the existing scaling laws in controversy. A consistent non-dimensional representation of the results provided offer sufficient grounds for judgment on their own.

The selection of NaCl and KCl for this study was dictated by a number of reasons; the properties of these compounds are very well known, well-defined nanometer sized hydrophilic particles are of interest not only in aerosol studies and instruments calibration, but also they could be used as a vehicle (coating or matrix form) for compounds in targeted drug delivery.

EHDA scaling laws

EHDA is feasible to generate highly monodisperse liquid droplets at a very stable frequency and thus of very stable and reproducible product concentrations. The size and the generation rate of liquid droplets produced with this method depend on a series of parameters: (i) the liquid properties such as surface tension, viscosity, conductivity, and dielectric constant, and (ii) the operating parameters such as liquid flow rate and electrical field applied and acting at the capillary tip. All of those parameters determine the electrospray behavior and impact the generated droplet size.

Several previous electrospray studies introduced and experimentally confirmed scaling laws describing the electrospray process and related the liquid properties and the operating parameters to diameter of the generated droplets (Rosell-Llompart and de la Mora 1994; Fernandez de la Mora and Loscertales 1994; Gañán-Calvo 1999, 2004; Gañán-Calvo et al. 1994, 1997; Chen et al. 1995; Chen and Pui 1997; Lenggoro et al. 2000; Basak et al. 2007; Fernandez de la Mora 2007). It was experimentally found that the ratio of the droplet diameter to the jet diameter remains nearly constant in cone jet mode (Cloupeau and Prunet-Foch 1989; 1990), since the most probable capillary breakup wavelength is not significantly altered when the flow rate [or electrical Weber number, López-Herrera and Gañán-Calvo (2004)] is kept below a critical range of values. Fernandez de la Mora and Loscertales (1994) proposed that the cone breakdown and jet emission was associated with the charge relaxation length $r^* = (Q\tau)^{1/3}$ where Q is the liquid flow rate and τ is the charge relaxation time $\tau = \epsilon\epsilon_0 / K$; ϵ is the relative permittivity, ϵ_0 is the permittivity in vacuum, and K is the specific conductivity of the solution (Fernandez de la Mora and Loscertales 1994; Rosell-Llompart and de la Mora 1994; Chen et al. 1995). Using this proposition, the jet diameter and consequently the droplet size D_d could be scaled as:

$$D_d = G \left(\frac{\epsilon\epsilon_0 Q}{K} \right)^{\frac{1}{3}} \tag{1}$$

where G may be a function of the relative permittivity, surface tension σ , density ρ , and viscosity of the solution. Fernandez de la Mora and Loscertales attempted to compare their proposition with experiments

using ethylene glycol, and represented the ratio of their measured diameter with their proposed scaling (1). They found a dispersion of values for the prefactor G ranging from about 0.55–0.85, which they considered acceptable in the absence of a better theoretical model. In reality, the undetermined nature of G in expression (1) left opened the issue of whether a closed scaling law for the droplet size or jet diameter could eventually be found, at least in a relatively ample range of parametrical values (liquid properties and flow rate). According to their proponents, expression (1) and its theoretical background assumed (Fernandez de la Mora 2007) that for sufficiently small Reynolds numbers (or high liquid conductivities), the self-similarity of Taylor’s solution should break down when the characteristic residence time of the liquid in a region with characteristic size $\sim \left(\frac{\epsilon\epsilon_0 Q}{K} \right)^{\frac{1}{3}}$ around the apex was of the order of the electrical relaxation time of the liquid. The authors assumed that the basic, quasi-electrostatic balance of the normal electric field and surface tension could only be broken by a limitation in the charge supply to the apex from which the jet issues, a mechanism that should be determined by charge relaxation. This understanding is suggested in Fig. 6 of Fernandez de la Mora and Loscertales (1994), where the authors drew a sketch with a perfect cone joined to a nearly cylindrical jet, pointing to an abrupt transition from cone to jet. In summary, the theoretical considerations of Fernandez de la Mora and Loscertales were mainly focused on the cone and the possible mechanisms determining its giving way to the issuing jet.

Alternatively, Ganan-Calvo focused his attention on the issuing jet to seek for possible alternative, close scaling laws for its characteristic diameter. To this end, he focused on the jet dynamics (Gañán-Calvo 1997a, b, 1998) under the action of an applied electric field whose intensity was proportional to that provided by Taylor’s solution. Thus, he proposed a general scaling of the equations of mass, momentum, and charge balance at the jet, leading to a scaling law for the characteristic jet diameter d_j as:

$$d_j = \left(\frac{\rho\epsilon_0 Q^3}{\sigma K} \right)^{\frac{1}{6}} \tag{2}$$

In that scaling (Gañán-Calvo 1997a, 1999; 2004; Gañán-Calvo and Montanero 2009), the conspicuous absence of the liquid polarity and the different exponent affecting the flow rate was subject of a hot

debate in the literature (Gamero-Castaño and Hruby 2002; Fernandez de la Mora 2007) that lasted until very recently (Gañán-Calvo and Montanero 2009) (to avoid repetitions, the interested reader can see this latter reference for a detailed formulation and discussion of the scaling law). This scaling law was found to be applicable for EHDA of all liquids reported in prior literature, where the droplet size can be expressed as:

$$D_d = k \left(\frac{\rho \varepsilon_0}{\sigma K} \right)^{\frac{1}{6}} Q^{\frac{1}{2}} \quad (3)$$

with $k \simeq 1.2$ within errors below $\pm 15\%$.

With the appropriate charge reduction, EHDA can be applied for defined transfer of solid, non-ionic, and soluble substances such as sucrose from liquid solutions into the airborne state. In this case the residue particle diameter d_p can be found by a simple mass balance relationship between D_d and d_p :

$$d_p = D_d \left(\frac{MC}{1000\rho} \right)^{\frac{1}{3}} \quad (4)$$

This expression can be applied to either Eq. (1) or (3) to yield:

$$d_p = G \left(\frac{\varepsilon \varepsilon_0}{K} \right)^{\frac{1}{3}} \left(\frac{MC}{1000\rho} \right)^{\frac{1}{3}} Q^{\frac{1}{2}} \quad (5)$$

or

$$d_p = k \left(\frac{\rho \varepsilon_0}{\sigma K} \right)^{\frac{1}{6}} \left(\frac{MC}{1000\rho} \right)^{\frac{1}{3}} Q^{\frac{1}{2}}, \quad (6)$$

respectively, where ρ is the density, C is the molar concentration, and M is the molecular mass of the substance that should be aerosolized.

Expression (1) was experimentally tested for sucrose solutions in ultrapure water with trace amounts of nitric acid to control the conductivity of the solutions by Chen et al. (1995), and is commonly applied to measure the size of the initial droplet diameter generated with electrospray (Chen et al. 1995; Laschober et al. 2006). Some facts may have led to an acceptable comparison of (1) with experiments: (i) a clear determination of the exponent affecting Q in the droplet size can be shaded by experimental noise and uncertainties, (ii) the exponents 1/3 in (1) and 1/2 in (2) are relatively proximal within the an order of magnitude for the non-dimensional variable Q/Q_s ,

assuming experimental errors, (iii) the exponent affecting the liquid polarity ε in (1) is small, and (iv) the hypotheses made in the reconstruction of the originally electrosprayed droplet size strongly affects the results if the solute is an electrolytic salt or yields ionic components in solution.

In this work, we aim to test the applicability of either (1) or (3) to predict the droplet size in the case of high liquid conductivities and polarities, leading to nanometer-range sizes. In case of strong electrolytic solutions the concentration has an eminent impact on the conductivity. For the description of the electrospray process of electrolytic solutions Basak et al. (2007) developed a modification to the before mentioned scaling law (1). The resulting scaling law substitutes the specific conductivity K in Eq. 4 by the equation for the dependency of the specific conductivity to the precursor concentration. For strong electrolytes this dependency was given by the Kohlrausch empirical expression and it was proposed that the particle diameter scaled as $d_p \propto Q^{1/3} (\lambda_0 - bC^{1/2})^{-1/3}$, where b was an empirical constant and λ_0 was the equivalent conductivity at infinite dilutions. Interestingly, those authors used hypothesis (i) given in the Introduction: the electrospray process does not modify the chemical composition of the electrosprayed droplets. As a noteworthy remark, that hypothesis is fundamentally inconsistent with the argument used by Fernandez de la Mora (2007) in support of his scaling law: that the liquid bulk becomes nearly deprived of one of the ionic species at the cone-jet neck, which freezes and determines the value of the issued electric current and the jet diameter.

For the two salts investigated in this work the relationship between molar concentration and conductivity was found to be linear, as expected for strong electrolytes. Following either (1) or (2), the droplet diameter can be scaled with the $-1/3$ or the $-1/6$ power of the conductivity for identical liquid flow rates, respectively. Because of the linear relationship between concentration and conductivity, D_d should also be in a proportional relationship with the $-1/3$ or the $-1/6$ power of the molar concentration, respectively. Consequently, D_d could be scaled with $Q^{1/3}/C^{1/3}$ or with $Q^{1/2}/C^{1/6}$. The only consistent way to assess the validity of one or the other is finally a representation of data in terms of non-dimensional variables involving the relevant physical parameters.

Experimental

Materials

NaCl, KCl, sucrose, ammonium acetate, and sterile filtered water (W3500) were all purchased from Sigma Aldrich (St. Louis, MO, USA). Both salts—NaCl and KCl—have been diluted in aqueous ammonium acetate buffer liquids at different ammonium acetate concentrations, or in pure water. The concentrations of salts—electrolytes—in a liquid obviously affect the conductivities of the solutions. The conductivities of the resulting concentrations have been measured at a temperature of 22 °C with a conductivity meter (Lf318, WTW GmbH). All concentrations and conductivities are listed in Table 1. The surface tension has been measured for different NaCl concentrations in both buffer liquids using the capillary effect of the liquid in a thin capillary with a cathetometer. It has been found that the changes are small for the investigated concentration ranges. From now on, both surface tension and viscosity have been considered independent from the concentration and close to the values for pure water. This is in agreement with data found in the literature (Li et al. 1999; Zhang and Han 1996).

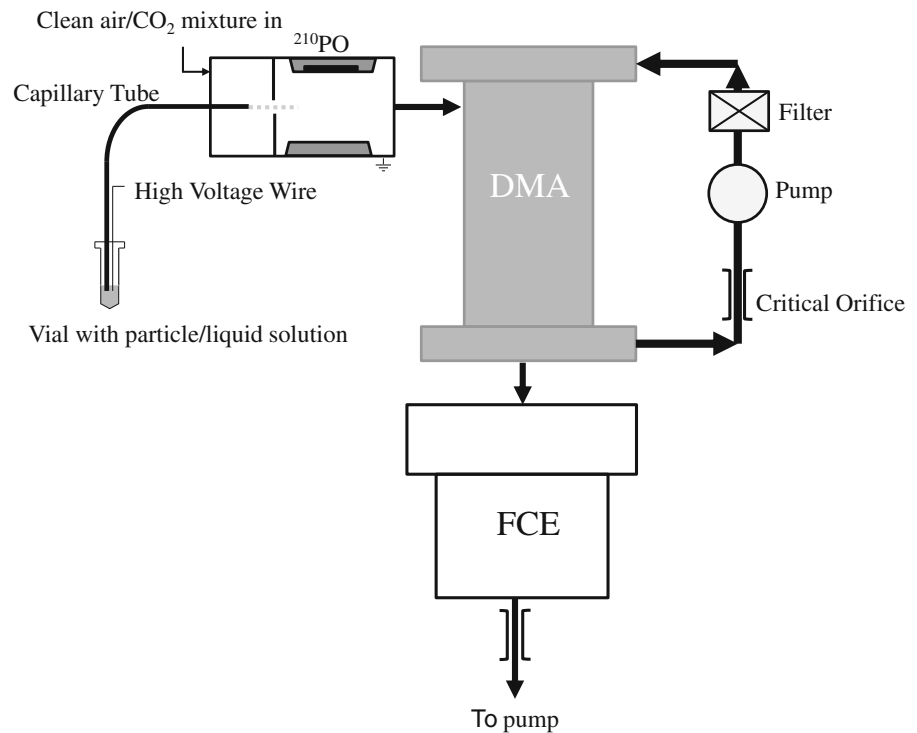
Table 1 List of all solutions used for NaCl and KCl showing the buffer liquids and the resulting conductivities

Concentration (mM)	Buffer liquid	Conductivity (mS/cm)
NaCl		
11.93	Water	1.5
3.18	9 mM AmAc in water	1.46
12.7 mM AmAc in water	1.41	
0.68 referred to as (**)	13.4 mM AmAc in water	1.43
0.942	15 mM AmAc in water	1.7
2.57	Water	0.29
4.76	Water	0.515
9	Water	0.91
KCl		
8.72	Water	1.2
1.74	Water	0.23
0.87	Water	0.12
0.87 referred to as (*)	15 mM AmAc in water	–
Sucrose		
0.092	20 mM AmAc in water	2
0.18	20 mM AmAc in water	2
0.46	20 mM AmAc in water	2
0.92	20 mM AmAc in water	2

Experimental procedure

A schematic of the experimental setups used is shown in Fig. 1. The aerosol generation is performed using a commercial electrospray device (TSI Inc., electrospray aerosol generator EAG, model 3480). Mobility distributions have been measured with a custom-made Vienna type nano differential mobility analyzer (nDMA) (Allmaier et al. 2008). A custom-made Faraday cup electrometer (FCE) has been used as a detection device.

The EAG is operated with a capillary of 25 μm inner and 150 μm outer diameter and a length of 25 cm. The liquid flow rate can be adjusted by changing the pressure across the capillary. The dependency of pressure to liquid flow rate can be calculated using the equation for Poiseuille flow in a circular tube (Batchelor 1967). In the measurements presented here the liquid flow rate throughout the capillary has been varied in a range from 53.5 to 71.4 nL/min. The EAG has been operated in stable cone-jet mode for all experiments and a positive voltage has been applied to the liquid at the tip of the capillary for generation of initially highly positively charged aerosol droplets. The highly charged droplets emerging from the capillary tip are exposed to bipolar ions

Fig. 1 Experimental setups

generated by a weak radioactive radiation (^{210}PO , alpha radiation). The dry particles after completed liquid evaporation exit the electrospray device in a steady-state charge equilibrium (Boltzmann–Fuchs equilibrium) in which most particles are neutral and a small fraction of the particles is carrying \pm one charge (Fuchs 1963). In the size range considered here the probability of particles carrying two or more charges is practically negligible.

The EAG uses a mixture of dry, purified, particle-free, clean air and CO_2 introduced around the capillary tip to transport the droplets emerging from the tip to the charging chamber for charge reduction and then out of the instrument through its aerosol outlet. The instrument is operated typically at flow rates of about 1.5 L/min of clean and dry air and 0.3 L/min CO_2 . The CO_2 is necessary for spraying liquids of high surface tension to increase the electrical break down limit of the gas and avoid corona discharge (Tang and Gomez 1994; López-Herrera and Gañán-Calvo 2004). The DMA used in this study operates at a sheath flow rate of 20 L/min determined by a critical orifice. A negative high voltage is applied to the inner electrode of the instrument to measure the size distribution of the positively charged fraction of particles generated in the EAG. The voltage difference between the inner

and the outer electrode is in a linear relationship to the particle electrical mobility using geometric and flow parameters of the DMA (Winklmayr et al. 1991). From the electrical mobility the particle equivalent diameter can be determined using the Stokes–Millikan equation (Tammet 1995). For measurements of mobility distributions of the generated aerosol the FCE is mounted directly on the DMA outlet to keep the distances short and thus minimize losses of the small highly diffusive particles. The aerosol flow through the DMA and the FCE is set to 2.2 L/min determined by a critical orifice (Fig. 1).

Results and discussion

Dry particle diameter

It has been observed in our experiments that the diameters of dry aerosol particles generated by EHDA from solutions of identical concentrations and conductivity evidently increase with an increase of the liquid flow rate as predicted by the scaling laws (1), (3), and (4) and confirmed in many previous studies. The effect of the applied electrical field has been found to produce a minimal impact in mobility diameter and

aerosol concentration. Increasing the applied voltage led to a slight decrease in mobility diameters. These small shifts observed here were, however, negligible compared to the width of the peaks in the mobility diameter distributions measured with the DMA. Lenggoro et al. (2000) found that in cone-jet mode increasing the voltage at the capillary tip led to a minor increase in the mobility diameter of the generated aerosol particles. In the works of Chen et al. (1995), or Rosell-Llompart and Fernandez de la Mora (1994) it has been found that the residue particle diameter was nearly independent from the applied voltage. Following these observations in our experiments the ES-voltage has been kept constant at 2 kV.

Figure 2 shows the measured mobility diameter distributions of electrospray generated airborne NaCl and KCl particles after liquid evaporation sprayed from solutions of different conductivities. The liquid flow rate for all measured size distributions in this graph has been kept at a constant value of 71.4 nL/min. The full width at the half maximum (FWHM) of the measured peaks varies between 20 and 24 %. The slight lift shoulder of the leading edge of measured distributions (around relative concentrations of about 0.1) that can be seen to the left of the main peaks in distributions are caused by particles carrying two elementary charges (doubly charged particles) which cannot be resolved with the DMA instrument used for these experiments. The lift shoulder emerges at half of the voltage of the main peak indicating that the

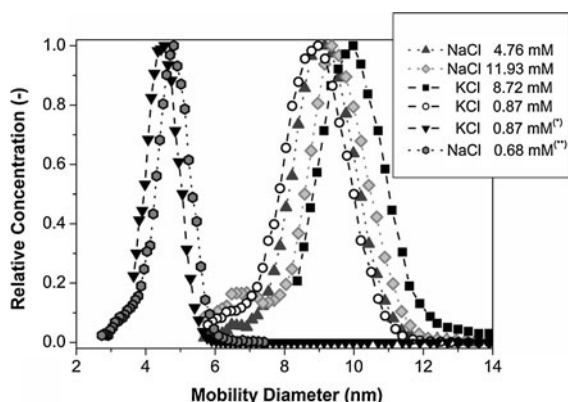


Fig. 2 Measured mobility size distributions of NaCl and KCl aerosol particles obtained from electrospraying solutions of different concentrations and conductivities, (*) and (**) stand for KCl and NaCl solutions in water with ammonium acetate, see also Table 1, all spectra are measured for a liquid flow rate of 71.4 nL/min

particles are of the same mobility diameter but doubly charged. This has been confirmed also by a tandem DMA experiment, described in detail in the literature (see for example Hummes et al. 1996; Reischl et al. 1996; Wild et al. 2012; Attoui et al. 2013); the data of the tandem experiment are not shown in this manuscript). Under the operational conditions of the electrospray the presence of doubly charged particles in the size range investigated here is possible due to the low Nt product (where N is the number of ion pairs and t is the residence time of the particles in the neutralization zone) in the chamber. The carrier gas flow rates have been kept rather high to minimize diffusional losses. This resulted in an incomplete neutralization process so that the particles did not reach Boltzmann charge equilibrium (Liu and Pui 1974; Fuchs 1963). These experiments confirmed that the particles generated with this method are fairly monodisperse in size but a small fraction of them may carry more than one elementary charge.

The particles generated have been found to be monodisperse over the entire investigated size range. The particle concentration besides the peaks has been found to be practically zero for all size distributions. This indicates clean conditions and no influence of background particles from the solvent on the measured size distributions. However, for high particle mobilities (small diameters) a rise in concentration has been found. This is caused by air ions from the polonium source inside the electrospray instrument which is used for particle neutralization.

The generation of monodisperse cluster particles from liquid solutions with EHDA is only possible in a system where concurrent with the decreasing size of the evaporating droplet its electrostatic charge decreases due to the presence of bipolar carrier gas ions (the charge reduced system). This way the charge to mass ratio is kept below the Rayleigh limit (Kaufman and Dorman 2008; Scalf et al. 1999). The high monodispersity of the generated particles in the way that no smaller particles have been observed confirms that the Coulombic explosions of the initially generated droplets has been successfully avoided in the aerosol generation process (Chen et al. 1995). It should be noted here that charge neutralization by bipolar carrier gas ions necessarily involves the incorporation of ions from the gas into the droplet. Consequently, the chemical composition of the droplet is necessarily altered with respect to the original

solution. This has never been seriously considered in prior literature, assuming that the excess ions in the droplet over the neutral concentration of cations and anions from the original solution was always negligible. In this work, this hypothesis is revised: in the following sections we will show that existing scaling laws for the emitted electric current and droplet size [either (1) or (2)] point to a non-negligible excess of one of the ionic species in the droplet (either anions or cations depending on the voltage polarity used) when its size is in the nanometer range.

In contrast to solutions of sucrose, both NaCl and KCl show electrolytic behavior. This causes that variation in the salt concentrations in pure water, which leads to changes in the conductivity of the solution. The initial electrospayed droplet diameter of solutions with non-electrolytic behavior does not depend upon the concentration of the precursor in the solution and on the conductivity of the solution. The opposite behavior is found for electrolytes and can be easily explained by Eq. (1) or (3).

The molar concentration range and, therefore, also the conductivity range investigated in our experimental work has been limited between 0.7 and 12 mM for both salts. For very low molar concentrations stable spraying conditions were not achieved which is associated with the low conductivity of the solutions. For very high concentrations precipitation of salt has been observed at the capillary tip and led to subsequent plugging of the capillary.

The electrolytic behavior of the NaCl and KCl solutions is plotted in Figs. 3 and 4, respectively. It can be seen that with increasing salt concentration the

conductivity of the solution increases linearly. For constant liquid flow rates of 71.4 nL/min for NaCl and KCl the measured particle diameters are plotted in the same graphs. It can be seen that the particle diameters are within $\pm 3\%$ for all measured NaCl and $\pm 8\%$ for all measured KCl concentrations. The deviations for the different concentrations are small compared to the FWHM of the measured size distributions indicated by the error bars in Figs. 3 and 4. This is a consequence of the electrolytic behavior: increasing the conductivity of the solutions leads to a decrease of the initial droplet diameter which should lead to smaller dry particle diameters. However, increasing the conductivity of the solutions requires an increase of salt concentration in the solution which evidently has to result in increasing dry particle diameters. From the experimental data it can be seen that within the experimental uncertainties both effects cancel each other out which in consequence leads to the constant diameter measured for dry particles.

Consequently, it can be stated that in order to generate salt particles over a wide size range the conductivity of the buffer liquid has to be controlled in a different way than by varying the salt concentration. As general principles, the initial droplet diameter and the molar concentration of salts in the liquid have to be kept small in order to produce small particles (see Eqs. 5 and 6). However, small initial droplet diameters require a high conductivity. In order to increase the conductivity without increasing the molar concentration of salt in solution, the buffer liquid has to be changed. This has been done in this work by adding varying amounts of ammonium acetate to the

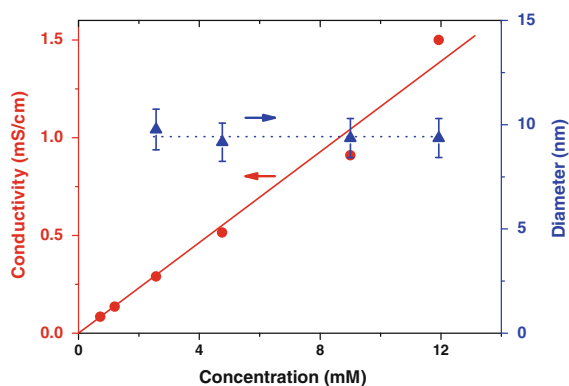


Fig. 3 Concentration to conductivity relationship for NaCl including measured particle diameters, all spectra are measured for a liquid flow rate of 71.4 nL/min

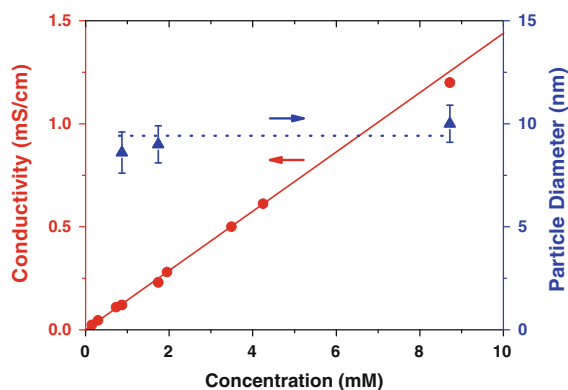


Fig. 4 Concentration to conductivity relationship for KCl including measured particle diameters, all spectra are measured for a liquid flow rate of 71.4 nL/min

solutions. (see Table 1—first 4 lines). Ammonium acetate is a volatile salt that evaporates with the water (in the absence of electrochemical reactions) and thus it could be argued that its concentration would not affect the particle diameter of the generated dry salt particles (Kaufman and Dorman 2008).

With our experiments we were able to generate aerosol particles in a size range between 3 and 10 nm for different NaCl and KCl solutions and varying liquid flow rates in the range from 53.5 to 71.4 nL/min.

The accuracy of the particle size measurement is associated with the resolution of the DMA instrument. This has been measured with two identical nDMAs in series [tandem experiment, Hummes et al. (1996)]. For the nDMA used in this study the uncertainty in particle size measurement is less than 5 % in the investigated particle size range. The other determining parameter in terms of uncertainty in the scaling law is the liquid flow rate in the capillary. All experiments have been performed with the same capillary. Therefore, the statistical error of the liquid flow rate is determined by the pressure drop applied between the capillary inlet and its tip. The total statistical experimental error of the liquid flow rate is also less than 5 % in this case.

In the next sections, we revise these issues involved in the calculation of the original droplet size.

Original droplet diameter

The indirect determination of the original droplet diameter from the measured dry particle size (Eq. 4) carries some difficulties fundamentally associated to the electrochemical processes taking place in electro-spray. We first tried to reproduce the experimental results for sucrose to confirm the experimental results by Chen et al. (1995). We used a 20 mM ammonium acetate in water solution as a buffer liquid and added different concentrations of sucrose. The conductivity was kept constant at a value of 2 mS/cm. At this point, when the dominant solute concentration is made of a low electrochemically active or inactive chemical, one may follow the approach of Chen et al. (1995), assuming that the chemical composition of the electro-sprayed residues is the same as that of the original solution. This same assumption was undertaken in prior works as in Lenggoro et al. (2000) or Basak et al. (2007) to calculate the droplet diameter using Eq. (4).

However, the assumption that the composition of the dry and solid particles is preserved from the precursor salt in liquid solution when strong electrolytes are involved is clearly questionable, given the electroosmotic relative migration of the ionic species in the issuing nano-jet under the strong applied electric field necessary to achieve the cone-jet electro-spraying conditions. Indeed, the excess ion concentration (high charge excess) at the droplet demanded by the cone-jet electro-spray process may become comparable to the ionic salt concentration present in the bulk. This is the case not only when using single-component solutions of salts like NaCl or KCl, but also when using sucrose with the addition of an electrolyte like ammonium acetate. Thus, more rigorous hypotheses on electrochemical alterations of the droplet composition are needed.

In the following, we compare the calculations assuming that chemical composition is preserved, with alternative calculations based on hypotheses involving electro-spray physics and the ulterior neutralization processes.

Results assuming preserved chemical composition

In this section, we assume that the chemical composition of droplets is unaltered by the electro-spraying process and ulterior neutralization. In this case, we simply use Eq. (4) to calculate the original droplet diameter. Figure 5 shows the experimental results for the droplet diameter plotted as a function of the flow rate, being both variables written in a classical non-

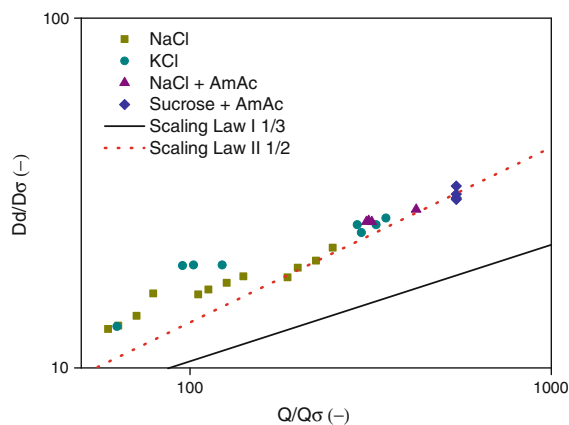


Fig. 5 Plot of results under the assumption of unaltered chemical composition from original solution to droplet (no electrochemical effects)

dimensional form (see for example Gañán-Calvo and Montanero 2009) as:

$$Q/Q_\sigma = \frac{\rho Q K}{\sigma \varepsilon_0}, \quad D_d/d_\sigma = \left(\frac{\sigma \varepsilon_0^2 D_d^3}{\rho K^2} \right)^{1/3} \quad (7)$$

It should be noted that the electrical permittivity of the liquid is absent in this non-dimensionalization. For those concerned on the potential importance of this parameter in the scaling laws and the possible inconsistency of utilizing (7) for a legitimate comparison, however, we note that its value is kept constant in this work, $\varepsilon = 81$, given that the solvent is water and the solute concentrations are sufficiently low to neglect their influence on the permittivity of the solution. Thus, a full comparison of experimental data with both (1) and (2) in a 2D plot using the two non-dimensional variables (7) is completely consistent in this work.

First, the global trend (general slope) of the experimental data points might be compatible with the scaling law I by Fernandez de la Mora et al. (dashed line, Fernandez de la Mora and Loscertales 1994, p. 160; Eq. 1). In this case, the pre-factor G_G in a scaling law as $D_d/d_\sigma = G_G (D_d/d_\sigma)^{1/3}$ should be $G_G = G\varepsilon^{1/3} = 4.33G$. The G values obtained by Fernandez de la Mora (see Fernandez de la Mora and Loscertales 1994, p. 160) ranged from about 0.55–0.8, which yields G_G values from 2.4 to about 3.5, respectively. Besides, Chen, Pui and Kaufman (1995) obtained a fitting with $G = 0.36 \rightarrow G_G = 1.56$. This evident dispersion in the values of the scalar prefactor among the different authors points to an inherent inconsistency that cannot be attributed to experimental errors alone or the possible influence of the applied voltage (most authors have shown that the influence of the latter is negligible, as previously discussed). In reality, pre-factors are as important as the exponents in scaling laws when the investigation takes place in the non-dimensional realm. Notwithstanding, in Fig. 5 we have represented the scaling law I, simply taking an average value $G_G = 2.25$ between both groups of authors. If a line with their presumed slope (1/3) was fitted to our droplet diameter calculations following their same working hypotheses, its pre-factor should be clearly in disagreement with those obtained by both prior authors groups. On the other hand, the plot also shows deviations of the data from the scaling law II proposed by Gañán-Calvo and coworkers (Gañán-Calvo 1997a, 1999, 2004; Gañán-Calvo and

Montanero 2009, Eq. 3, black dashed line) for smaller values of Q/Q_σ . In summary, under the assumption that chemical composition is preserved, the overall calculated original droplet size is in general above both existing theoretical predictions, although scaling law II shows better agreements.

Results assuming electrochemical alteration of the particle composition

As previously anticipated, the formation of charged droplets necessarily involve the electroosmotic migration of ionic species along the cone-jet liquid domain. In the absence of direct measures of the chemical composition of the resulting droplets, a highly challenging endeavor on itself, we resort to theoretical considerations and propose a set of realistic electrochemical hypotheses to close the problem. In summary, we propose that the final chemical composition of the droplets can be calculated under the following hypotheses:

1. The number of excess charges N_q per droplet can be calculated from well-established scaling laws for the issued electric current, and the droplet size. Given that $\varepsilon = 81$ for all solutions in this work, we can use the expression $I \simeq 2.5 (\sigma K Q)^{1/2}$ (Fernandez de la Mora and Loscertales 1994; Gañán-Calvo 1999, 2004; Hartman et al. 1999) to obtain:

$$N_q = \frac{\pi D_d^3 I}{6 Q e} \simeq 1.3 \frac{D_d^3}{e} \left(\frac{\sigma K}{Q} \right)^{1/2} \quad (8)$$

where e is the elementary charge. The ionic species making up most of the charge excess at the droplet surface would be that with the larger electric mobility among the different ionic species (electrolytes) with the polarity corresponding to the one used in the experiments (in our case, those cations with larger mobility among the ionic species present).

2. The bulk solution remains nearly unaltered in accord with the leaky dielectric model (e.g. Saville 1997). Thus, the concentration of neutralized ionic (dissociated electrolytes) and neutral species would be the same as the one in the original solution.
3. We assume that neutralization in the ambient atmosphere (air + CO₂) involves the formation of compounds after adsorption of ambient gases

(CO₂) and radicals produced under the shower of α-rays from the ²¹⁰PO source (such as CO₃²⁻, NO₃⁻, NO₂⁻, O²⁻, and the like). An inspection of well-established data tables in the literature (e.g. Lide 2007) shows that the larger (negative) formation enthalpies among carbonates, nitrates, nitrites, oxides, etc. for all cations present in our experiments (v.g. Na⁺, K⁺; we assume that NH₄⁺ readily evaporates) belong to carbonates. Therefore, under the assumption that CO₃²⁻ is the dominant gas ion finally incorporated into the droplet to neutralize the excess charge due to either Na⁺ or K⁺ we can then easily calculate the final volumetric concentration of the different species in the droplet before evaporation. To do so, we can express the volume of the solid salt residues as:

$$\frac{\pi D_d^3}{6} \sum \frac{C_i M_i}{\rho_i} + \frac{M_q N_q}{z_q \rho_q N_A} = \frac{\pi d_p^3}{6} \tag{9}$$

where C_i is the concentrations of the i—species and subindex q stands for the carbonate. N_A is the Avogadro number and z_q = 2 for carbonates.

Under these hypotheses, the reconstructed droplet diameter can be finally calculated from the particle diameter as:

$$D_d = \left(\sum \frac{C_i M_i}{\rho_i} + \frac{M_q I}{z_q F \rho_q Q} \right)^{-1/3} d_p \tag{10}$$

where F = N_Ae is Faraday number. We have represented those alternative calculations in Fig. 6. The new

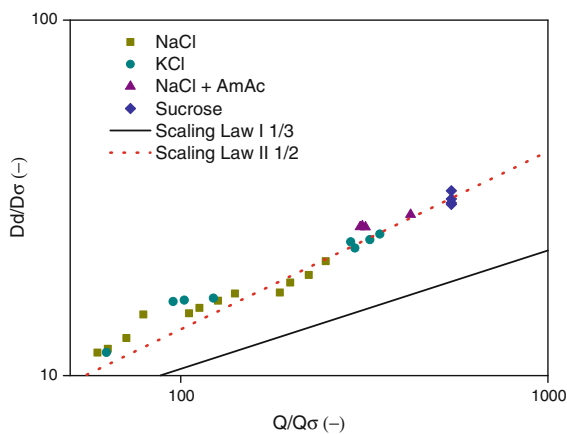


Fig. 6 Plot of results under the assumption of electrochemical effects

droplet sizes now appear to be in good agreement with scaling law II. Here, we emphasize that *we have not fitted* our data to that scaling law: the values both the prefactor (1.3) and the power (1/2) used are taken from the ones originally proposed in Gañán-Calvo 1997a, 1999, 2004 and Gañán-Calvo and Montanero 2009. Moreover, that prefactor covers the entire existing experimental data collections in the literature (Gañán-Calvo and Montanero 2009) with typical deviations smaller than about ±15 %, in contrast with the large scatter of values of the prefactor of scaling law I in published studies.

Conclusion

EHDA has been applied to generate NaCl, KCl, and sucrose aerosols. The EHDA device has been operated in cone-jet mode for all described experiments. The following conclusions can be drawn from the experimental results:

1. It has been found that the size range for residue particles generated by salt solutions in pure water is limited to a very narrow size range around 10 nm. In order to achieve smaller sizes different buffer liquids with higher conductivity than the highly diluted salt in water solutions need to be used. In our case we used buffer liquids containing different concentrations of ammonium acetate in pure water, which increases the conductivity without having any impact on the resulting particles size of the dry particle. With this method particles as small as 2.5 nm can be produced with charge reduction electrospray.
2. We have compared the original droplet sizes corresponding to the measured particle diameters with two existing scaling laws due to (i) Fernandez de la Mora and co-workers Fernandez de la Mora and Loscertales (1994), scaling I; and (ii) Ganán-Calvo and co-workers (Gañán-Calvo 1997a, 1999, 2004; Gañán-Calvo and Montanero 2009), scaling II. To do that, the original droplet diameters have been indirectly calculated following two alternative hypotheses: (i) assuming that the chemical composition of the droplets is unaltered by the electrospraying process (this has been assumed in the works by Lenggono, de la Mora, Chen and co-workers), and (ii) assuming that the electrospray process

produces an electrochemical migration of specific ionic species to accommodate the measured excess charge in the droplets. While the former hypothesis yields to relatively poor agreement with both scaling laws I and II, the latter provides droplet sizes showing a good agreement with scaling law II.

Eventually, gaining full understanding of the process will yield a control over electrochemistry in the electrospray resulting in broader utilization of the method in physics and chemistry.

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References

- Allmaier G, Laschober C, Szymanski W (2008) Nano ES—GEMMA and PDMA, new tools for the analysis of nanoparticles—protein complexes, lipoparticles, and viruses. *J Am Soc Mass Spec* 19:1062–1068
- Attoui M, Fernández-García J, Cuevas J, Vidal-de-Miguel G, Fernandez de la Mora J (2013) Charge evaporation from nanometer polystyrene aerosols. *J Aerosol Sci* 55:149–156
- Bacher G, Szymanski W, Kaufman S, Zöllner P, Blaas D, Allmaier G (2001) Charge-reduced nano electrospray ionization combined with differential mobility analysis of peptides, proteins, glycoproteins, noncovalent protein complexes and viruses. *J Mass Spec* 36(9):1038–1052
- Basak S, Chen D, Biswas P (2007) Electrospray of ionic precursor solutions to synthesize iron oxide nanoparticles: modified scaling law. *Chem Eng Sci* 62(4):1263–1268
- Batchelor GK (1967) An introduction to fluid dynamics. Cambridge University Press, Cambridge
- Chen D, Pui D (1997) Experimental investigation of scaling laws for electrospraying: dielectric constant effect. *Aerosol Sci Technol* 27(3):367–380
- Chen DR, Pui DYH, Kaufman SL (1995) Electrospraying of conducting liquids for monodisperse aerosol generation in the 4 nm to 1.8 μm diameter range. *J Aerosol Sci* 26:963–977
- Cloupeau M (1994) Recipes for use of EHD spraying in cone-jet mode and notes on corona discharge effects. *J Aerosol Sci* 25(6):1143–1157
- Cloupeau M, Prunet-Foch B (1989) Electrostatic spraying of liquids in cone-jet mode. *J Electrost* 22:135–159
- Cloupeau M, Prunet-Foch B (1990) Electrostatic spraying of liquids: main functioning modes. *J Electrost* 25(2):165–184
- Fernandez de la Mora J (2007) The fluid dynamics of Taylor cones. *Annu Rev Fluid Mech* 39:217–243
- Fernandez de la Mora J, Loscertales I (1994) The current emitted by highly conducting Taylor cones. *J Fluid Mech* 260:155–184
- Fuchs N (1963) On the stationary charge distribution on aerosol particles in a bipolar ionic atmosphere. *Pure Appl Geophys* 56(1):185–193
- Gamero-Castaño M, Hruby V (2002) Electric measurements of charged sprays emitted by cone-jets. *J Fluid Mech* 459:245–276
- Gañán-Calvo AM (1997) Cone-jet analytical extension of Taylor's electrostatic solution and the asymptotic universal scaling laws in electrospraying. *Phys Rev Lett* 79:217–220
- Gañán-Calvo AM (1997) On the theory of electrohydrodynamically driven capillary jets. *J Fluid Mech* 335:165–188
- Gañán-Calvo AM (1998) The universal nature and scaling law of the surface charge in electrospraying. *J Aerosol Sci* 29:S975–S976
- Gañán-Calvo AM (1999) The surface charge in electrospraying: its nature and its universal scaling laws. *J Aerosol Sci* 30:863–872
- Gañán-Calvo AM (2004) On the general scaling theory for electrospraying. *J Fluid Mech* 507:203–212
- Gañán-Calvo AM, Montanero JM (2009) Revision of capillary cone-jet physics: electrospray and flow focusing. *Phys Rev E* 79:066305
- Gañán-Calvo AM, Lasheras JC, Dávila J, Barrero A (1994) The electrostatic spray emitted from an electrified conical meniscus. *J Aerosol Sci* 25:1121–1142
- Gañán-Calvo AM, Dávila J, Barrero A (1997) Current and droplet size in the electrospraying of liquids scaling laws. *J Aerosol Sci* 28:249–275
- Hartman RPA, Brunner DJ, Camelot DMA, Marijnissen JCM, Scarlett B (1999) Electrohydrodynamic atomization in the cone-jet mode physical modeling of the liquid cone and jet. *J Aerosol Sci* 30:823–849
- Hummes D, Neumann S, Fissan H, Stratmann F (1996) Experimental determination of the transfer function of a differential mobility analyzer (dma) in the nanometer size range. *Part Part Syst Charact* 13(5):327–332
- Jaworek A, Sobczyk A (2008) Electrospraying route to nanotechnology: an overview. *J Electrost* 66:197–219
- Kaufman S, Dorman F (2008) Sucrose clusters exhibiting a magic number in dilute aqueous solutions. *Langmuir* 24(18):9979–9982
- Laschober C, Kaufman S, Reischl G, Allmaier G, Szymanski W (2006) Comparison between an unipolar corona charger and a polonium-based bipolar neutralizer for the analysis of nanosized particles and biopolymers. *J Nanosci Nanotechnol* 6(5):1474–1481
- Lenggoro I, Okuyama K, Fernándezde la Mora J, Tohge N (2000) Preparation of ZnS nanoparticles by electrospray pyrolysis. *J Aerosol Sci* 31(1):121
- Li Z, Li Y, Lu J (1999) Surface tension model for concentrated electrolyte aqueous solutions by the Pitzer equation. *Ind Eng Chem Res* 38(3):1133–1139
- Lide DR (2007) Handbook of chemistry and physics, 88th edition. CRC Press, Boca Raton
- Liu B, Pui D (1974) Electrical neutralization of aerosols. *J Aerosol Sci* 5(5):465–472
- López-Herrera JM, Gañán-Calvo AM (2004) A note on charged capillary jet breakup of conducting liquids: experimental validation of a viscous one-dimensional model. *J Fluid Mech* 501:303–326
- Reischl GP, Makela JM, Karch R, Neced J (1996) Bipolar charging of ultrafine particles in the size range below 10 nm. *J Aerosol Sci* 27:931–949

- Rosell-Llompart J, de la Mora JF (1994) Generation of monodisperse droplets 0.3 to 4 micrometre in diameter from electrified cone-jets of highly conducting and viscous liquids. *J Aerosol Sci* 25:1093–1119
- Saville DA (1997) Electrohydrodynamics: the Taylor–Melcher leaky dielectric model. *Annu Rev Fluid Mech* 29:27–64
- Scalf M, Westphall MS, Krause J, Kaufman SL, Smith LM (1999) Controlling charge states of large ions. *Science* 283:194–197
- Tammet H (1995) Size and mobility of nanometer particles, clusters and ions. *J Aerosol Sci* 26(3):459–475
- Tang K, Gomez A (1994) Generation by electrospray of monodisperse water droplets for targeted drug delivery by inhalation. *J Aerosol Sci* 25(6):1237–1249
- Taylor G (1964) Disintegration of water drops in electric field. *Proc R Soc Lond A* 280:383–397
- Wild M, Meyer J, Kasper G (2012) A fast accurate method of using electrical mobility scans for the direct measurement of aerosol charge distributions. *J Aerosol Sci* 52:69–79
- Winklmayr W, Reischl GP, Lindner AO, Berner A (1991) A new electromobility spectrometer for the measurement of aerosol size distributions in the size range from 1 to 1000 nm. *J Aerosol Sci* 22(3):289–296
- Zeleny J (1917) Instability of electrified liquid surfaces. *Phys Rev* 10:1–6
- Zhang HL, Han SJ (1996) Viscosity and density of water + sodium chloride + potassium chloride solutions at 298.15 K. *J Chem Eng Data* 41:516–520