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The mass transfer at Taylor cones

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ABSTRACT

Electrospraying is a highly attractive method for generation of small particles and also for measurement applications of particles in suspensions. In the cone jet mode, the particle generation rate increases with decreasing flow rate. For applications in the field of aerosol technology flow rates of less than 10µl/h are attractive as particle sizes of less than 200nm can be obtained in this flow rate range. At the same time generation frequency of drops reaches the values required for size measurements by Scanning Mobility Particle Sizers (SMPS). A special challenge in operation of electrosprays at small flow rates is the change of liquid composition due to mass transfer processes between the Taylor cone and the surrounding gas phase. Typically used organic solvents such as alcohols, acetone or acetonitrile evaporate fast (or even evaporate completely) and mixtures containing such volatile species will change their composition significantly due to evaporation from the Taylor cone. Based on key experiments we show

a) that the evaporating solvent can be reduced by as much as a factor of 20 by controlling the gas phase saturation. This allows spraying volatile solvents such as e.g. methanol at flow rates down to less than 1µl/h and makes the attractive sub-10µl/h flow rate range accessible to quite volatile solvents as well.
b) that changes in the liquid composition by not considering the mass transfer (evaporation) problem lead to significant differences in liquid properties between the feed liquid and the Taylor cone. For example, an increase of surface tension by a factor of 2 is observed for water and t-butanol feed liquid.
c) that employing a saturated sheath gas flow allows for very effective manipulation of the solvent composition in the Taylor cone. Based on water as feed liquid we show that a sufficient amount of organic solvent is easily transferred to the Taylor cone liquid from the gas phase to allow spraying the water without electron scavenging gases.

Measurement results of the Taylor cone liquid composition are in good agreement with predictions by the presented new model describing the mass transfer between the Taylor cone and the surrounding gas phase. The efficiency of the mass transfer, the predictability of the process and the opportunity of comparably quick changes of the Taylor cone liquid by changing the gas phase saturation state result in a powerful tool for the entire field of electrospraying at low rates.

1. Introduction

Electrosprays are widely used in different scientific applications: The electrospray is established as one of the most utilized ion sources in mass spectrometry allowing to transfer comparably large species such as proteins from a liquid into the gas phase as multiply charged ions. In aerosol, pharmaceutical and material science, the electrospray is used to generate narrowly distributed

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Symbols

A_1	a constant
c_D	drag coefficient of the spray capillary in m^3
$c_{p,gas}$	heat capacity of the gas in J/kgK
D_v	diffusion coefficient of a solvent molecule in the gas phase in m^2/s
Δh_v	enthalpie of evaporation J/mol
I_{spray}	electric current of the spray in A
K	conductivity in S/m
k_B	Boltzmann-constant in J/K
$\dot{N}$	molar flow in mol/s
N_A	Avogadro number 1/mol
Nu	Nusselt-number
Pr	Prandtl-number
p_d	saturation vapor pressure in Pa
Δp	pressure drop over the capillary in Pa
p_∞	vapor pressure of solvent at large distance in Pa
Re	Reynolds-number
R_{line}	electrical resistivity of the connection between the HV supply and the Taylor cone in Ω
r_{cap}	outer radius of the spray capillary (at the tip) in m
S_{drop}	surface of a drop in m^2
T_d	temperature of the liquid surface K
T_∞	gas temperature at large distance in K
$\dot{Q}$	heat flow in W
R	gas constant J/molK
r	radius in m
r_i	inner radius of the spray capillary in m
Sc	Schmidt-number
Sh	Sherwood-number
t	time in s
U	electric potential of the Taylor cone in V
U_{source}	electric potential adjusted by the HV supply in V
$\dot{V}$	feed flow rate in m^3 /s
V_m	volume of a solvent molecule m^3
v	gas velocity m/s
x	molar fraction in mol/mol
Z	distance between Taylor cone and counter electrode in m
γ	surface tension in N/m
γ_{TC}	surface tension of the liquid in the Taylor cone in N/m
γ_{ref}	reference surface tension of the liquid in the Taylor cone in N/m
ε_0	vacuum permittivity in As/Vm
η_L	feed liquid viscosity in Pas
η_{gas}	gas viscosity in Pas
θ	tip angle of the liquid cone
λ_{gas}	thermal conductivity of the gas W/mK
ρ_{gas}	gas density in kg/m^3

airborne particles in the size range down to a few nanometers from either particle dispersions of solutions of non-volatile materials which can be deposited as thin films (Jaworek & Sobczyk, 2008) and for measurement of particles in dispersions (Lenggoro, Xia, Okuyama, & Fernandez de la Mora, 2002; Thajudeen, Walter, Srikantharajah, Lübbert, & Peukert, 2017).

From a theoretical point of view scaling laws have been developed for the Taylor cone-jet mode (e.g. Fernández de la Mora & Loscertales, 1994; Gañán-Calvo, 2004). The scaling laws correlate the liquid feed flow rate and liquid properties such as conductivity, surface tension, density, viscosity and permittivity to the current uptake of the spray and the drop size produced. Gañán-Calvo (2004) identified that from the point of liquid properties most sprays scale in the I,E-regime where drop size and current uptake are dominated by inertia and electrostatic suction as the most relevant case for low viscosity liquids. Fig. 1 shows drop diameters and drop emission frequencies expected in this scaling regime for a liquid having a density of 950 kg/m^3 at a constant current uptake of 80 nA by Gañán-Calvo's I,E-scaling law.

From a practical point of view operation in the flow rate range below 10 µl/h is recommended in many applications and especially in aerosol science for the following reasons:

1.1. Particle number concentration

From the point of aerosol measurement technology the SMPS is one of the most employed device to measure particles sizes in the sub 100 nm size range with good resolving power. Typical aerosol sample flow rates are in the range of a few ten cubic centimeters per second. High concentrations in the sampled gas in the range of $10^7 \ldots 10^8$ cm^{-3} might be (residence time dependent) the target number concentration with respect to coagulation. At typical sample flow rates of SMPS systems of 20 cm^3/s particle generation

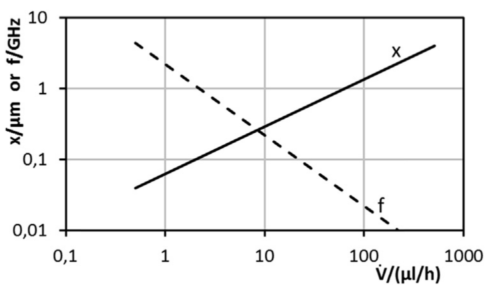

Fig. 1. Particle diameter x (solid line) and particle generation frequency f (dashed line) as function of the liquid flow rate according to the I, E-scaling suggested by Gañán-Calvo at a current of 80 nA and a liquid density of 950 kg/m^3.