The Effect of Molar Conductivity upon Current and Thrust in a Colloid Electrospray Thruster System.

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A high accuracy online flow rate measurement system has been used to determine the current flow rate scaling relationships for solutions of triethylene glycol and sodium iodide over a rage of conductivities from 0.0025S/m – 0.016S/m in high vacuum conditions. The current flow rate trends for these solutions were found to exhibit a power law relationship similar to that described by previous researchers where *I* (the electrospray current) is proportional to *Q* (the volumetric flow rate) to some power *a*. However the exponent *a* of the current flow rate trends were found to differ from the theoretical predictions reported in the literature. A study including data from literature revealed the exponent of the current flow rate trends to be sensitive to the molar conductivity of the sprayed solution. We conclude that when evaluating the potential performance achievable using specific electrolytic solutions as propellants, in order to have accurate predictions of the potential thrust from a colloid electrospray thruster system, it is necessary to evaluate the solution molar conductivity rather than the conductivity.

Nomenclature

a	=	power law exponent
$f(\varepsilon_r)$	=	empirically derived parameter
I	=	ES current
$\dot{m}$	=	mass flow rate
Q	=	volumetric flow rate
q/m	=	charge to mass ratio
T	=	Thrust
V	=	thruster acceleration voltage
γ	=	fluid surface tension
ε_r	=	relative permittivity
ε_0	=	permittivity of vacuum
K	=	fluid conductivity
Λ_m	=	molar conductivity
μ	=	fluid viscosity
ρ	=	fluid mass density

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I.   Introduction

The electrospray (ES) process has been identified[1-3] as a potential means of electrostatic propulsion at the micro-Newton level for the past decade or so. These devices, termed colloid ES thrusters, utilize the mode of ES known as cone-jet mode. In this mode a spray of highly charged droplets is produced. These are then accelerated in a static electric field to produce the required thrust. The advantages of this system over more established FEEPs systems are the lower applied voltages, lower power and the potential for higher thrust stability[4]. Full and detailed characterization of the spray properties identifies the need for further experimental data obtained under high vacuum conditions. One of the most important properties required in support of the design of a colloid ES thruster is the spray current and the scaling of this current with the emitted fluid volumetric flow rate. This is immediately apparent when considering the thrust, which is principally determined by time averaged droplet charge to mass ratio, q/m, and may be written as,

$$T = \dot{m}v_e \approx \dot{m}\sqrt{2\frac{q}{m}V} = \dot{m}\sqrt{2\rho IQV} \tag{1}$$

where $\dot{m}$ is the mass flow rate, v_e is the droplet stream velocity, V is the voltage applied to accelerate the droplets, I is the emitted current, Q is the volumetric flow rate and ρ is the propellant mass density.

The most widely used current flow rate scaling relationships are those of F. de la Mora[5] and Gañán-Calvo[6] they give current scaling as

$$I = f(\varepsilon_r)\left(\frac{\gamma K Q}{\varepsilon_r}\right)^{\frac{1}{2}} \tag{2}$$

$f(\varepsilon_r)$ is an empirically determined function and

$$I = 6.2\left(\frac{\gamma K Q}{(\varepsilon_r - 1)^{\frac{1}{2}}}\right)^{\frac{1}{2}} - 2I_0 \tag{3}$$

where $I_0 = \gamma\left(\dfrac{\varepsilon_0}{\rho}\right)^{\frac{1}{2}}$

The F. de la Mora model is based on the assumption of sink flow in the cone region and includes an empirically determined factor to bring experimental values in line with the theoretical predictions. The Gañán-Calvo model is derived from a one-dimensional flow model in the jet region combined with dimensional analysis.

While both models give good general approximations to the *I(Q)* scaling, they fail to elucidate fully the nature of this scaling. Perhaps in such a complex system a full understanding of the *I(Q)* scaling, including all parameters, may be difficult to achieve. However there is some scope for further analysis to gain a greater insight into the nature of this scaling. Chen and Pui[7] attribute the varying electrical permittivity functions which have been determined to collapse the *I(Q)* curves for various solutions to the use of various different additives to control solution conductivity, since different additives provide ions in solution with differing mobilities. They also note that since the total current through the system is the sum of both the surface convection current and the bulk solution ohmic current, the ion mobility can have a significant effect on spray current. One way of establishing the effect of ion mobility on *I(Q)* scaling is to examine the effect of solution molar conductivity, Λ_m. In a 1:1 electrolyte solution the molar conductivity can effectively be considered a measure of the sum of the mobilities of the positive and negative ionic species in solution.

As part of our own programme of colloid ES thruster development, we have paid particular attention to the need for high fidelity measurements of all the critical parameters affecting electrospray properties. In particular we have focused on overcoming the problems of direct measurement of the flow rate, in real time, throughout experiments, as the control conditions are changed. Indeed we have established a system that automatically logs the appropriate currents simultaneously with the flow rate[8]. The experimental configuration adopted for data reported in this paper permits unambiguous direct determination of the volumetric flow rate through the ES system. In particular the

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approach we have used avoids the ambiguity of pressure drop across the fluid meniscus by the simple expedient of determining the pressure drop along part of the fluid feed system, thus avoiding potential error sources that feasibly may underlie earlier published data. The experiments and results described in this paper aim to characterize the effects of flow rate, Q, solution conductivity, K, and molar conductivity Λ_m on the ES current. The results are based on the use of four solutions having different electrical conductivities, but having measured similar fluidic properties.

II.   Experimental Arrangement

A. Emitter Grid Assembly and Current Measurement

All the measurements reported here were recorded whilst electrospraying into a high vacuum pressure environment. The electrospray emitter used was a stainless steel capillary supplied by Coopers needle works. It has a right circular cross section with an inside diameter of 0.305mm and an outside diameter of 0.560mm. The emitter was mounted in a 1/16" stainless steel bulkhead union from SGE and sealed using a SilTite aluminium ferrule.

An extractor electrode, consisting of a 20mm diameter stainless steel disk with a 6mm central aperture was mounted in an insulating PTFE holder. The PTFE holder was supported in an optical mounting block on insulating rods and positioned at a distance of 3mm from the emitter front face. The centralized aperture was optically aligned on the axis of the emitter.

The emitter/extractor assembly was housed in a vacuum chamber, shown schematically in Fig. 1.The chamber was evacuated down to pressures below 10^{-3} mbar during testing using a turbo molecular pump (TMP) backed by a rotary vane pump (RVP). The currents on the emitter and extractor electrode were measured on-line by a custom built two stage optically isolated system[9]. This approach safely converted the signal from high voltage to a data logger at ground potential. A battery powered high voltage stage, floated at the same potential as the emitter, contains a current to voltage converter in the transresistance configuration. This system was designed to measure currents up to $\pm2\mu A$, with a voltage response of ~1mV/nA and a time response of 1s. This converter is then followed by a voltage to frequency converter for optical signal transmission. A fibreoptic cable connected to a frequency to voltage converter chip at ground potential comprises the second stage, which is then directly and safely connected to a PC for data logging. Such isolation is clearly required on the high voltage line to the emitter, but was also included on the extractor current monitor in order to protect instrumentation from any potential short circuit to high voltage. A CCD camera with zoom lens was used to establish the cone-jet mode of operation.
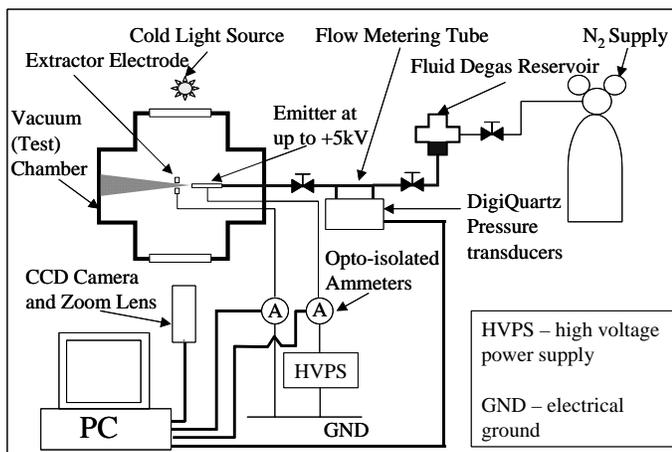

Figure 1. Electrospray experimental arrangement.

B. Fluid reservoir and feed system

A DN40 four-way cross from Caburn MDC was used as a fluid reservoir. An RVP connected to one arm of this cross enabled the reservoir to be evacuated. An inlet valve on the opposing arm allowed the reservoir to be pressurized with up to an atmosphere of N_2.The pressure in the reservoir was measured using a Bourdon gauge attached via a T-piece to the same arm as the RVP. An outlet valve on the base of the reservoir was attached to a capillary feed system, which allowed the fluid to flow into the spray chamber via a flow rate measurement system. A view port on the top of the reservoir allowed the fluid level to be monitored.

C. Electrospray solutions

The experiments detailed in this paper were carried out using solutions of triethylene glycol (TEG) doped with varying quantities of sodium iodide (NaI) to give a range of conductivities between 0.0025S/m –0.016 S/m.

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D. Flow meter design and description

The volumetric flow rate measurement was achieved by determining the pressure drop between a pair of high precision, absolute pressure transducers, within a limited section of the fluid feed pipe-work. The specific transducers selected are temperature compensated Paroscientific Digiquartz 740-23A quartz crystal pressure transducers. The accuracy of these is dependent upon the temporal resolution of the measurement; at a frequency of 1Hz, the adopted sample rate, the transducer accuracy is 1 part in 10^6. The measured pressure drop, ΔP, is directly proportional to the volumetric flow rate Q as described by the Poiseuille equation

$$Q = \frac{\Delta P \pi R^4}{8 \mu L} = \frac{\dot{m}}{\rho} \tag{4}$$

Where R is the internal radius of the pipe section and ΔP is the pressure change along length L of the pipe. Calibration was performed for each fluid used by measuring the mass of fluid collected over a period of time. The flow pipe setup used in this work gave an absolute volumetric flow rate accuracy of ~0.3nL/s and a resolution of 0.03nL/s. A more complete description of the instrument is provided in Smith[8].

E. High voltage power supply

The high voltage power supply (HVPS) used was a Canberra model 3105 with a range of +/-5kV. For the measurements reported here, this was connected in the positive mode to the stainless steel capillary via a tag connected to the SGE union.

III.   Results and Discussion

For the TEG + NaI solutions used in this paper the non-dimensional scaling equations of F. de la Mora and Gañán-Calvo are given as

$$\frac{I}{I_0} = 12 \left(\frac{Q}{Q_0} \right)^{\frac{1}{2}} \tag{5}$$

and

$$\frac{I}{I_0} = 13.68 \left(\frac{Q}{Q_0} \right)^{\frac{1}{2}} - 2 \tag{6}$$

respectively , where

$$Q_0 = \frac{\gamma \varepsilon_r \varepsilon_0}{\rho K}.$$

Figure 2. Non-dimensional scaling equations.

Figure 2 shows our non-dimensionalised experimental data obtained from solutions of TEG+NaI plotted alongside the non-dimensional equations of the F. de la Mora and Gañán-Calvo models. Clearly there is some discrepancy between both model predictions and the experimental data. A closer inspection of the exponent values of the least squares best fit line of the experimental data from Table 1 suggests a trend of increasing exponent values with decreasing solution conductivity. Looking at this trend in terms of solution molar conductivity is however of limited use as the variation in molar conductivity of the solutions tested is limited, as can be seen from Table 1. However by including data from the literature the range of molar conductivity values may be extended and a more insightful picture of the effect of this
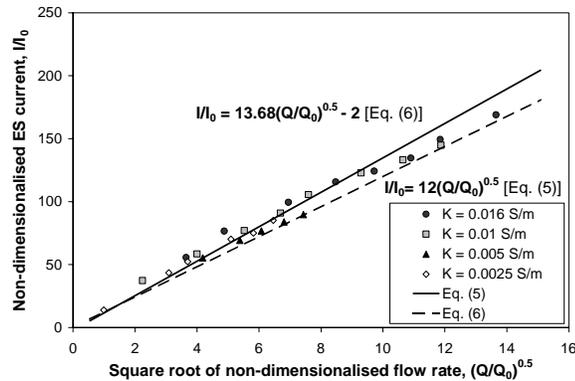
Table 1. Least squares best fit exponent values

K [S/m]	Λ_m [Scm^2/mol]	Least squares Best Fit exponent, a,
0.0025	1.588	0.46+/- 0.01
0.005	1.313	0.42+/- 0.01
0.01	1.199	0.42+/- 0.01
0.016	1.243	0.41+/- 0.02

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parameter on *I(Q)* scaling can be established. The data selected for inclusion from other researchers was based on organic solvents. Data that used water (H$_2$O) as a solvent was excluded because of the possible discrepancies caused by the unusual ion transport mechanism that can occur in water. Water is generally more easily dissociated than other solvents. The disassociation of water gives $2H_2O \Leftrightarrow H_3O^+ + OH^-$. Charge transport with H$_3$O+ and OH- ions results due to a mechanism known as the Grotthus mechanism. This differs from 'standard' ion transport mechanisms, since here charge transport is a result of the rearrangement of bonds in a long chain of water molecules. The rupture of an O-H bond in H$_3$O+ and formation of a new O-H bond in an adjacent water molecule results in charge movement. Thus, in this transport mechanism the ion does not physically move through the solution. The ion is therefore not subject to viscous forces of its ionic atmosphere.

The comparative data included in this study is from figure 8 of Ref. 5, for various lithium chloride (LiCl) doped solvents, with varying concentrations of LiCl. The exponents of the *I(Q)* relationship were taken as the slope of a least squares line of best fit through the experimental points. We note that this process may be subject to some small error, as we did not have the original source data.

Further data for our comparison is from the low conductivity work of Hartman[10] using ethylene glycol (EG) as the solvent. The exact concentrations of LiCl used by Hartman were not reported in Ref. 10, however in the case of ethylene glycol the concentration could be interpolated from a conductivity LiCl concentration plot obtained from the F. de la Mora[5]. The molar conductivities for n-Butanol and Methanol the two other solvents used in the Hartman paper were excluded from our analysis, as no available concentration: conductivity relationship could be found for these solutions.

It must be noted that both the Hartman and F. de la Mora data was taken for sprays conducted under atmospheric pressure in air. However F. de la Mora's research group concluded that the surrounding gas pressure has no effect on the current flow rate scaling[11,12].

Figure 3 shows the overall trend of *I(Q)* exponents vs. molar conductivity compiled from all the cited works, in addition to our own data. This shows clearly that when spray properties are plotted as a function of molar conductivity there is a distinctive trend. The trend shows an increasing *I(Q)* exponent with increasing molar conductivity. The least squares best-fit line for the data is given as $a = 0.051 Ln \Lambda_m + 0.413$ where a is the exponent value and Λ_m is the solution molar conductivity. The regression coefficient for this line is 0.928, which suggests a reasonable fit to the data. The exponent of the *I(Q)* curve can generally be thought of as a measure of

Figure 3. *I(Q)* **exponent as a function of molar conductivity**

the charge transfer efficiency of the cone-jet ES system. Clearly if the *I(Q)* exponent were to be unity, then there is a linear relationship between ionic dissociation as manifested by spray current and the flow of solution through the electrospray process. As the exponent decreases the system essentially becomes less efficient at transferring the available charge. The trend observed in Fig.3 indicates that this charge transfer efficiency into the charge spray is reduced with reducing electrical mobility of the charge carriers.
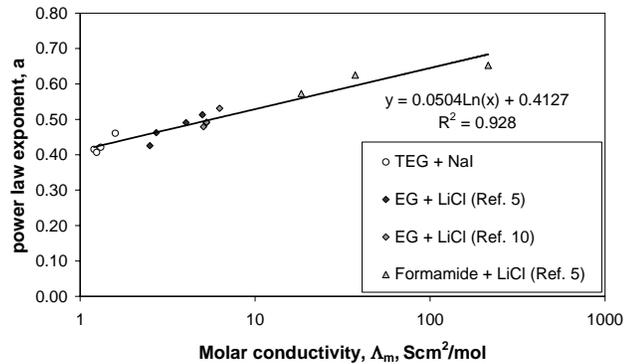
IV.   Conclusion

The data we have obtained, when compiled with previously published data, identifies that the stable spray properties of an electrospray are sensitive to solution molar conductivity rather than simply the measured conductivity. A core feature of any electric propulsion system is the propellant utilization efficiency. In the case of a colloid ES thruster one important factor underpinning utilization efficiency, is the way in which dissociated ions can be transferred into the spray itself, since it is only this capability that leads to the electrostatically generated thrust. This efficiency in a colloid ES thruster is sensitive to flow rate, as indicated by the exponent of the *I(Q)* relationship. Whilst the data presented here does not address the fundamental issue of the number of available ions in solution, indeed the liquids

we have investigated are unsuited to high specific impulse, we have revealed the importance of the molar conductivity upon relative efficiency in 1:1 electrolytic organic solutions. Improved performance will apparently be achieved using solutions of highest molar conductivity. The study presented in this paper now requires further expansion to include a greater variety of ionic species and solvents to fully understand the nature of the effect of charge carrier mobility on $I(Q)$ scaling.

Acknowledgments

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