Electrokinetic Phenomena in Concentrated and Porous Media

CBE/NE/BME 525

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Outline

1. Concentration effects.
2. Cell model – a simple approach to complex problems in concentrated dispersions and/or porous systems.
3. Shilov-Zharkikh cell model at low frequencies.
4. Electrophoretic mobility in concentrated dispersions.
5. Electroosmotic pumps.

Concentrated Systems

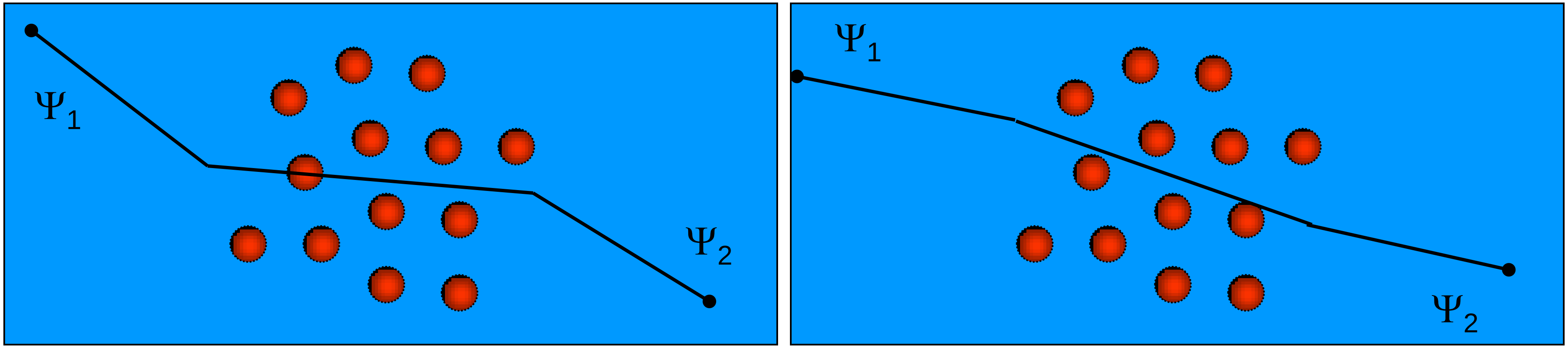
Smoluchowski, diluted systems $\mu_{\text{eo}} = -\dfrac{v_{\text{eo}}}{E}, \qquad \mu_{\text{ep}} = \dfrac{v_{\text{ep}}}{E}$

In a concentrated dispersion $E_{\text{ext}} \neq \langle E \rangle$

Externally applied field — Average field in the suspension

Then

$$v = \langle \mu \rangle \langle E \rangle, \qquad \langle \mu \rangle = \mu \frac{K_{\text{s}}}{K_{\text{mig}}^{0}}, \quad \text{or} \quad \langle E \rangle = \frac{K_{\text{mig}}^{0}}{K_{\text{s}}} E_{\text{ext}}$$



Maxwell-Wagner Theory: Volume Fraction Effects, Negligible Surface Conductivity

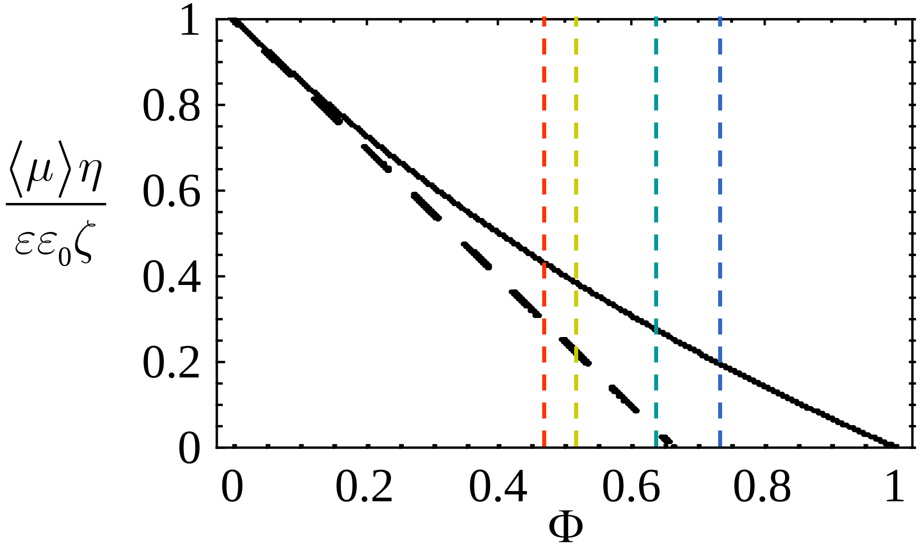
Criterion $$Du = \frac{K_{\mathrm{abs}}^{\mathrm{s}}}{RK_{\infty}} \rightarrow \text{Dukhin Number}$$

For *Du* << 1, the surface conductivity is unimportant

$$\langle \mu \rangle = \frac{\varepsilon \varepsilon_0 \zeta}{\eta} \left(\frac{1-\Phi}{1+\frac{1}{2}\Phi} \right)$$

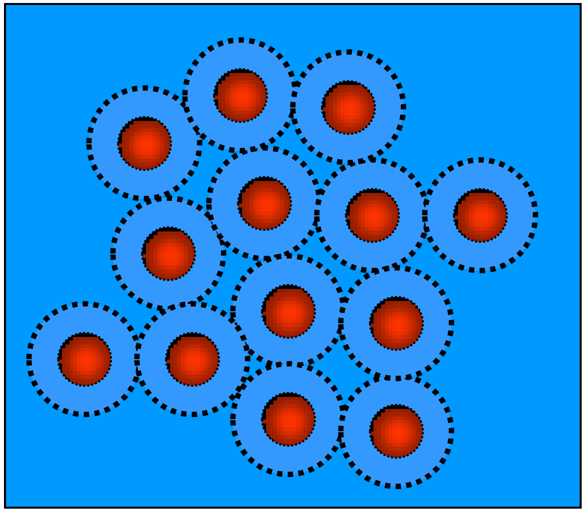
For low volume fraction

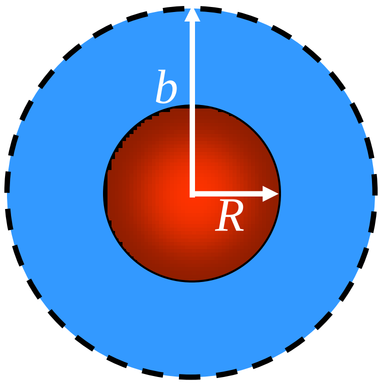
$$\langle \mu \rangle = \frac{\varepsilon \varepsilon_0 \zeta}{\eta} \left(1 - \frac{3}{2}\Phi \right)$$



Cell Model at Low Frequencies

Shilov & Zharkikh





$$\Phi = \left(\frac{R}{b}\right)^3$$

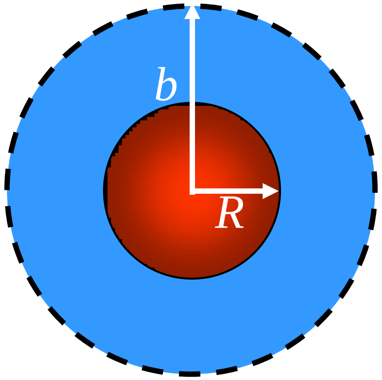
$$\omega << \omega_{\mathrm{h}} = \frac{2\eta}{\rho R^2} \text{ hydrodynamic relaxation}$$

$$\omega << \omega_{\mathrm{e}} = \frac{K^0_{\mathrm{mig}}}{\varepsilon\varepsilon_0} \text{ electrodynamic relaxation}$$

$$\omega << \omega_{\mathrm{c}} = \frac{2D}{R^2} \text{ DL polarization}$$

$$\omega << \frac{c}{R} \quad c \rightarrow \text{ speed of sound}$$

Cell Model: Governing Equations



Governing Equations for
$(b - R) > 1/\kappa$

$$\left.\begin{aligned} \eta\nabla^2 \mathbf{v} &= \nabla p \\ \nabla \cdot \mathbf{v} &= 0 \end{aligned}\right\} \text{ fluid motion}$$

$$\nabla^2 \Psi = 0 \quad \text{Laplace equation}$$

External potential

Solutions

$$v_r = \frac{D}{R}\cos\theta\left(A_1 - 2A_2\frac{R^3}{r^3} + 0.1A_3\frac{r^2}{R^2} + A_4\frac{R}{r}\right)$$

$$v_\theta = \frac{D}{R}\sin\theta\left(-A_1 - A_2\frac{R^3}{r^3} - 0.2A_3\frac{r^2}{R^2} - 0.5A_4\frac{R}{r}\right)$$

$$p = -\frac{D\eta}{R^2}\cos\theta\left(A_3\frac{r}{R} + A_4\frac{R^2}{r^2}\right)$$

$$\Psi = \frac{kT}{e}\cos\theta\left(A_5\frac{r}{R} + A_6\frac{R^2}{r^2}\right)$$

Cell Model: Boundary Conditions

Boundary Conditions

Particle surface

$$v_r\left(r=R\right)=0$$

$$v_\theta\left(r=R\right)=\frac{\varepsilon\varepsilon_0\zeta}{\eta}\left(\frac{\partial V}{\partial\theta}\right)_{r=R}$$

$$K_{\mathrm{mig}}^{0}\nabla V=\nabla_{\mathrm{S}}\cdot\mathbf{I}_{\mathrm{S}}$$

Cell Boundary (Kuwabara)

$$\left(\nabla\times\mathbf{v}\right)_{r=b}=\left(\frac{\partial v_\theta}{\partial r}+\frac{v_\theta}{r}-\frac{\partial v_r}{r\partial\theta}\right)_{r=b}=0$$

$$\left(\nabla p\right)_{r=b}=A_4\frac{3\eta D}{R^3}\Phi=0$$

$$\left(\frac{\Psi}{b\cos\theta}\right)_{r=b}=-E$$

Then

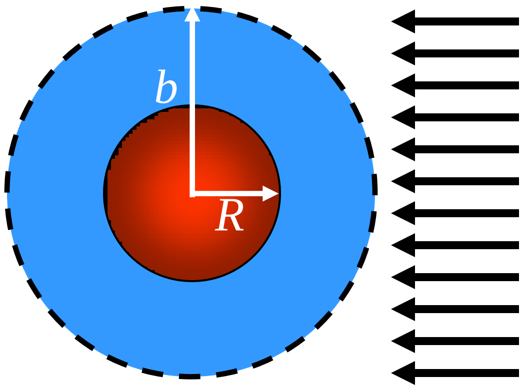
$$A_1=2A_2,\quad A_3=A_4=0$$

$$A_2=\frac{\varepsilon\varepsilon_0\zeta RE}{\eta D}\frac{1}{2\left(1+Du\right)+\Phi\left(1-2Du\right)}$$

$$A_5=2A_6\frac{1+Du}{1-2Du}$$

$$A_6=\frac{eRE}{kT}\frac{1-2Du}{2\left(1+Du\right)+\Phi\left(1-2Du\right)}$$

Fluid and Current Transport in the Cell



$$U = \left(\frac{v_r}{\cos\theta} \right)_{r=b} \quad \rightarrow \text{ average fluid flow}$$

$$I = -\left(\frac{K^0_{\text{mig}} \nabla_r \Psi}{\cos\theta} \right)_{r=b} \quad \rightarrow \text{ average current flow}$$

Kinetic coefficients

$$\langle \mu \rangle = \frac{\varepsilon\varepsilon_0 \zeta}{\eta} \frac{2\;\; 1-\Phi}{\left[2\;\; 1+Du\;\; +\Phi\;\; 1-2Du\;\right]}$$

$$\frac{K_s}{K^0_{\text{mig}}} = \frac{2\left[1+Du-\Phi\;\; 1-2Du\;\right]}{\left[2\;\; 1+Du\;\; +\Phi\;\; 1-2Du\;\right]}$$

Onsager Relationships in a cell are satisfied, hence (Saxen)

$$\frac{U}{E}_{\;\nabla p=0} = \frac{I}{\nabla p}_{\;E=0}$$

Some Useful Results Derived by Applying the Cell Model

Electric Current and Bulk EO Driven Flow in a Bead Microcolumn

Averaged Current vs Averaged Electric Field

S – cross sectional area

$$\frac{\langle I \rangle}{K_{\mathrm{mig}}^{0} S} = \langle E \rangle \left(\frac{1-\Phi}{1+\frac{1}{2}\Phi} \right)$$

EO Driven Bulk Fluid Flow vs the Averaged Field or Current

$$U = S\langle v_{eo} \rangle = S\frac{\varepsilon\varepsilon_0\zeta}{\eta}\langle E \rangle \left(\frac{1-\Phi}{1+\frac{1}{2}\Phi} \right) = \frac{\varepsilon\varepsilon_0\zeta}{\eta}\frac{\langle I \rangle}{K_{\mathrm{mig}}^{0}}$$

For given voltage, the electric current and bulk flow depend on the bead volume fraction, but do not depend explicitly on their size.

Electroosmotic Pressure

Combining the EO bulk flow expression with

$$U = \frac{SR^2}{3\eta\Phi\varphi \;\; \Phi}\frac{\Delta P}{L}$$

$$\varphi \;\; \Phi \;\; = \frac{3+2\Phi^{5/3}}{3- \;\; 9/2 \;\; \Phi+ \;\; 9/2 \;\; \Phi^{5/3}-3\Phi^2}$$

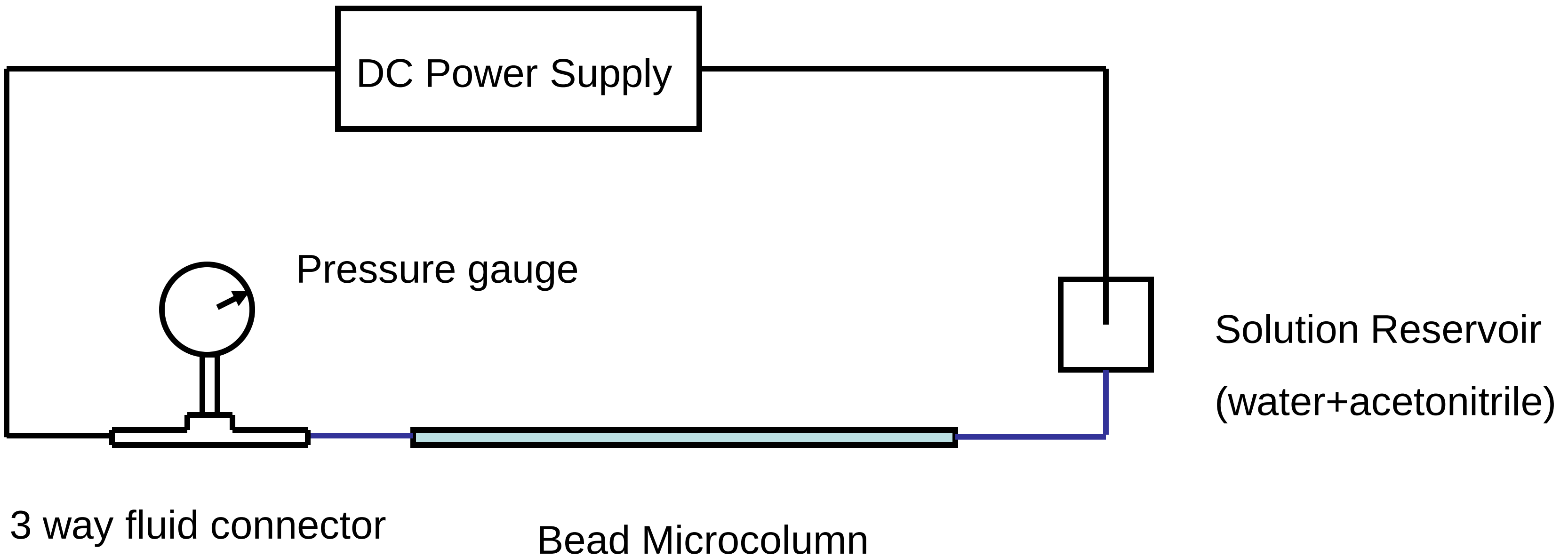
EO Pressure

$$\Delta P = \frac{3\varepsilon\varepsilon_0\zeta\Phi\varphi \;\; \Phi \;\; L}{R^2\lambda_0}\frac{\langle I\rangle}{S} = \frac{3\varepsilon\varepsilon_0\zeta\Phi\varphi \;\; \Phi}{R^2}\left(\frac{1-\Phi}{1+\frac{1}{2}\Phi}\right)L\langle E\rangle$$

The pressure depends both on the bead volume fraction and on their size

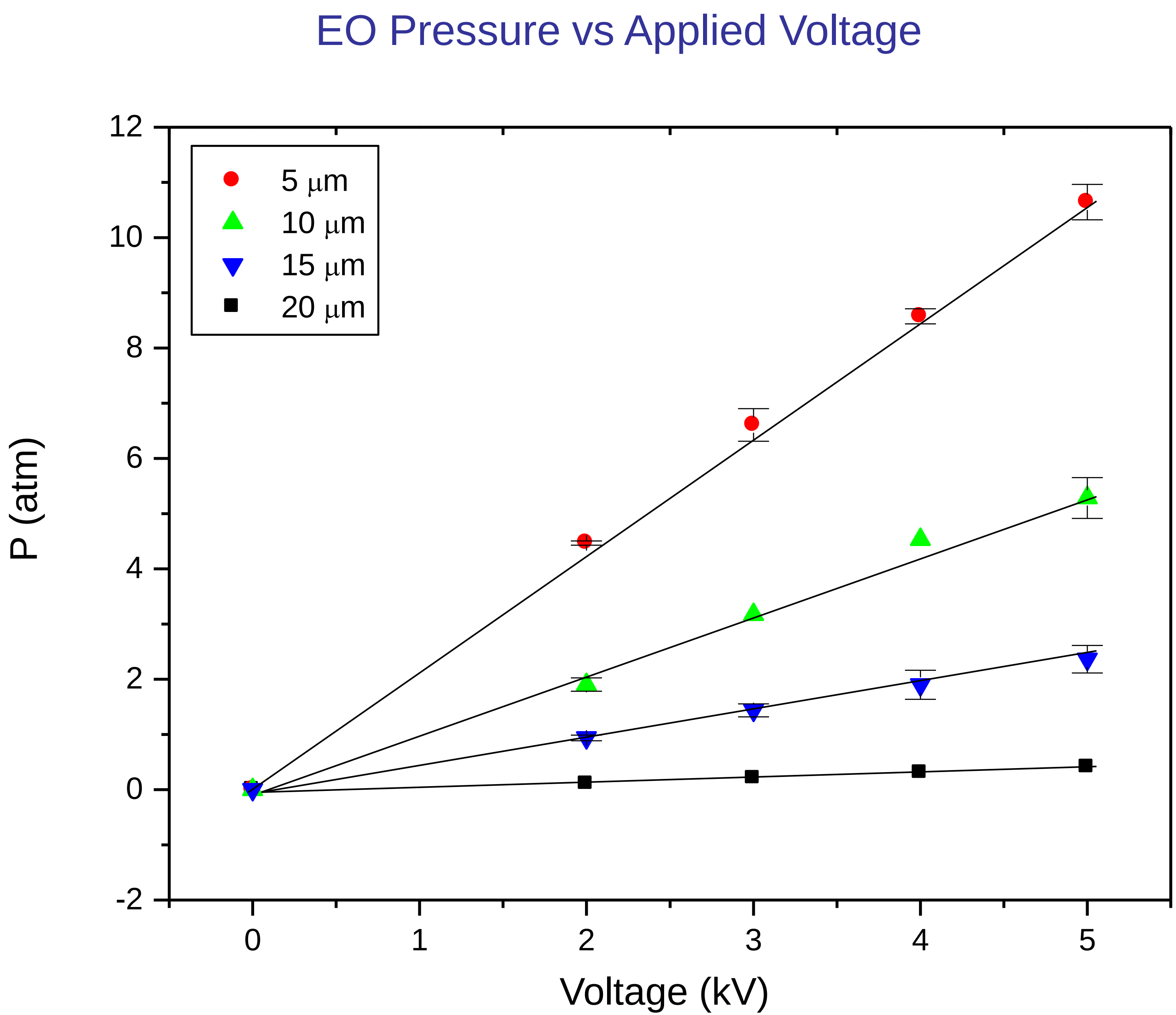
Pressure Experiments

Experimental Set-Up

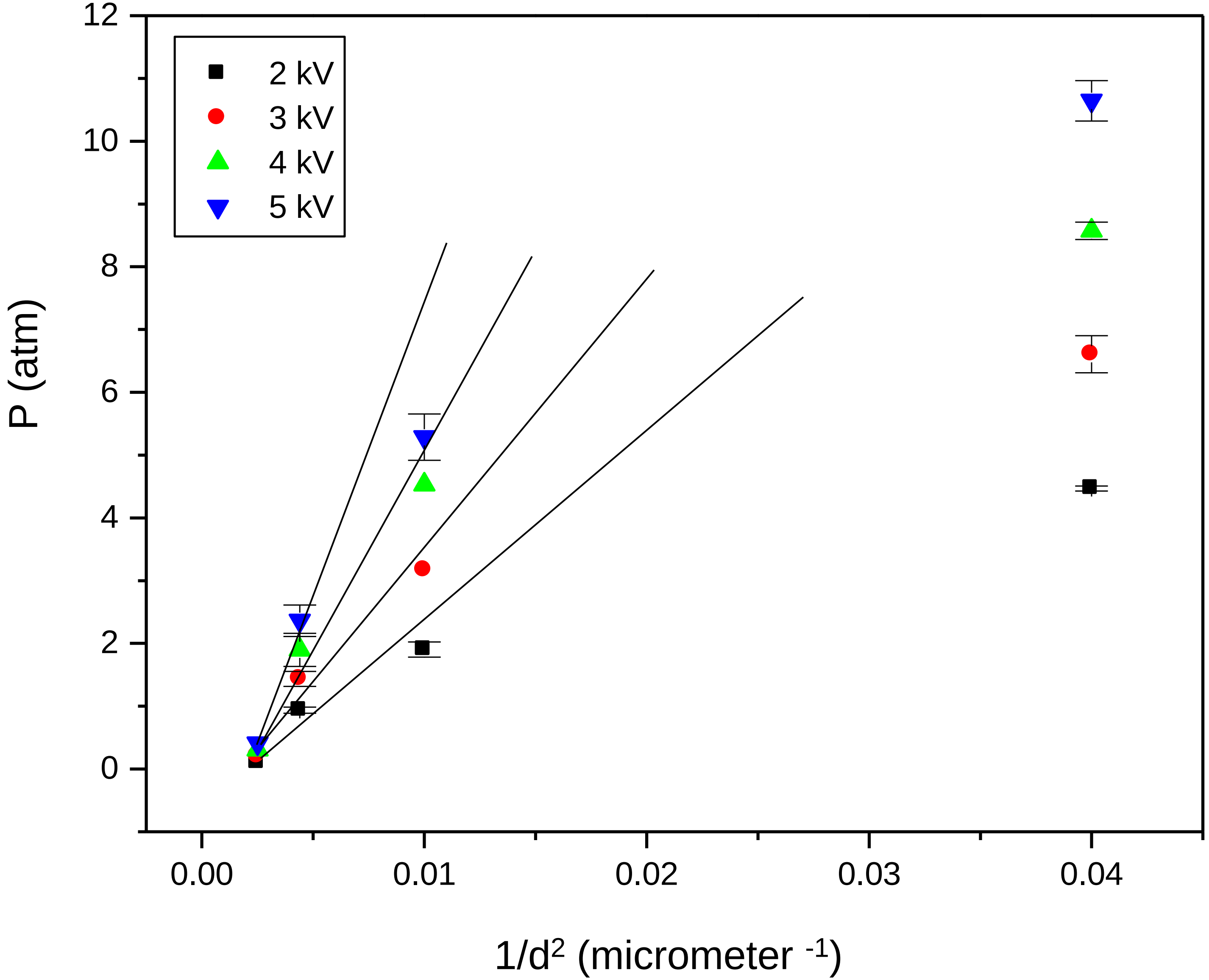


Column length is 6 cm

Column diameter is 400 microns


EO Pressure vs Applied Voltage
P (atm)
Voltage (kV)
5 μm
10 μm
15 μm
20 μm
12
10
8
6
4
2
0
-2
0
1
2
3
4
5

Pressure Dependence on the Bead Size



Conclusions

1. The average electrophoretic mobility using the cell model is reduced to the Smoluchowski result for $Du \ll 1$.
2. The model correlates with the Maxwell-Wagner theory
3. The cell model satisfies Onsager theorem and hence, yields the saxen relations.
4. The volume fraction dependence is in good agreement with the experiment.
5. The cell model presents a convenient theoretical approach for analysis of concentrated dispersions and porous media.
6. Packed bead microcolumns are a can be used as fluidic micropumps.