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Investigation of Seebeck effect in complex liquid electrolyte based thermoelectrochemical cells

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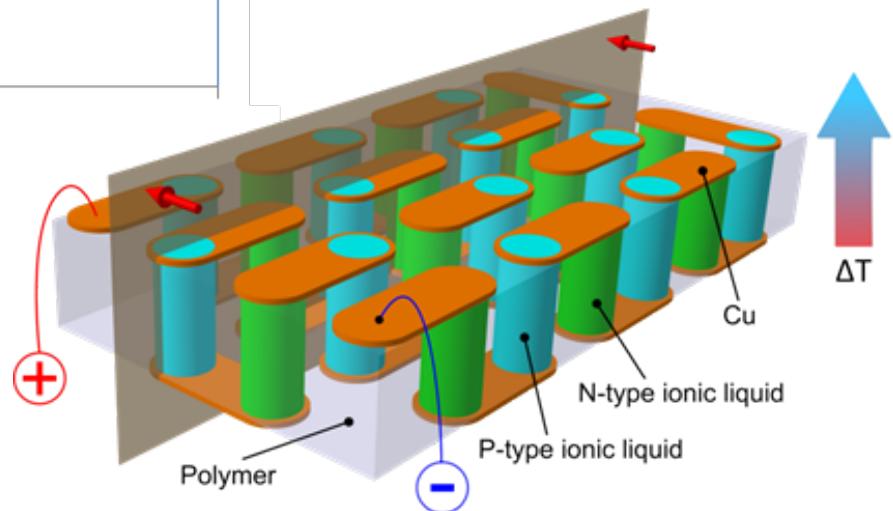
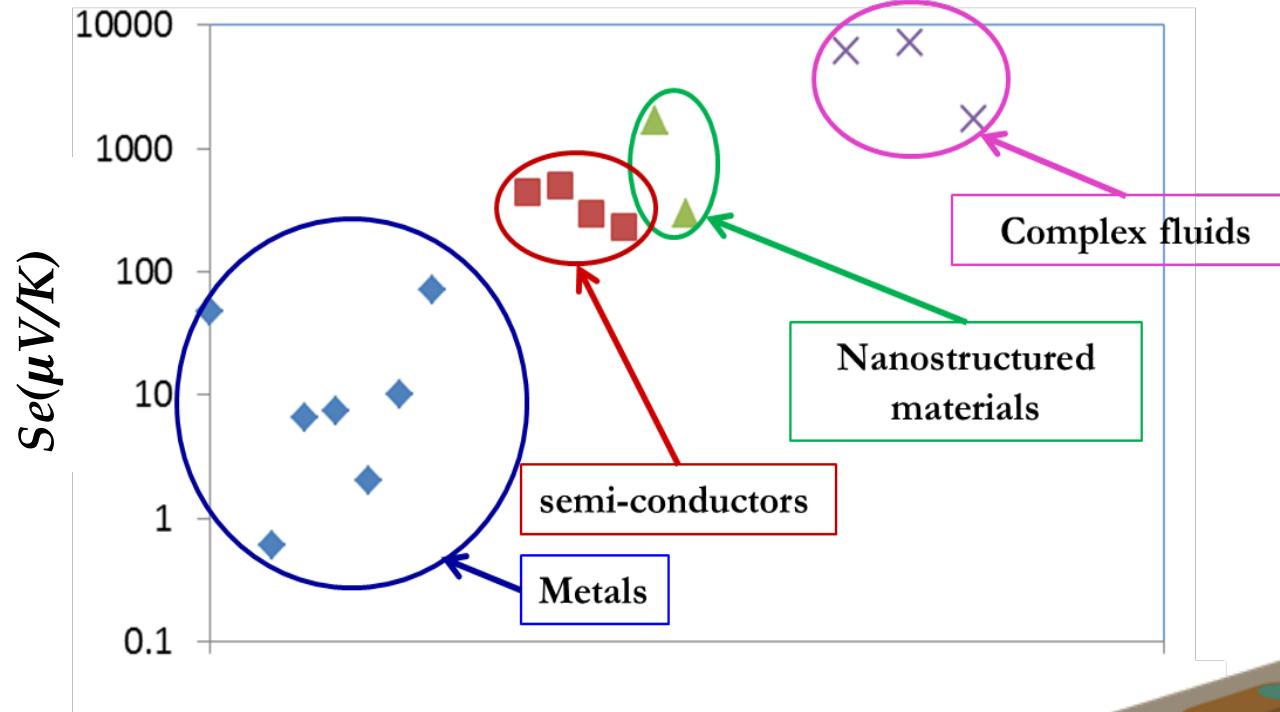
Conference on Modern Concepts and New Materials for Thermoelectricity, ICTP Trieste,
11th -15th March 2019

- Thermoelectricity in fluids
- Thermogalvanic cells
- Ferrofluid based thermogalvanic cells
- Ionic liquid based ferrofluids as thermoelectric materials
- Summary and Perspectives

Thermoelectricity in fluids

THERMOELECTRICITY IN COMPLEX FLUIDS

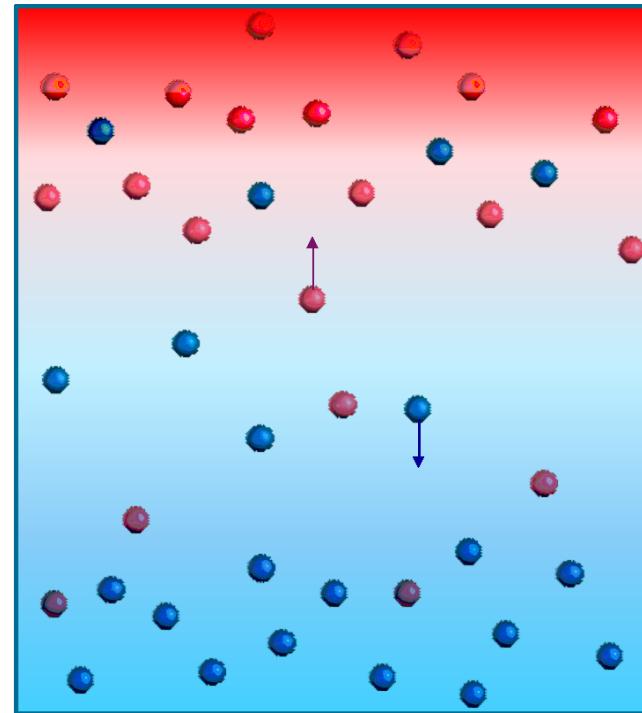
Se values for different materials



THERMOELECTRICITY IN COMPLEX FLUIDS

Bulk thermoelectric field, $\mathbf{E} = S\vec{\nabla}T$

where, S is Seebeck coefficient
and $\vec{\nabla}T$ is the thermal gradient



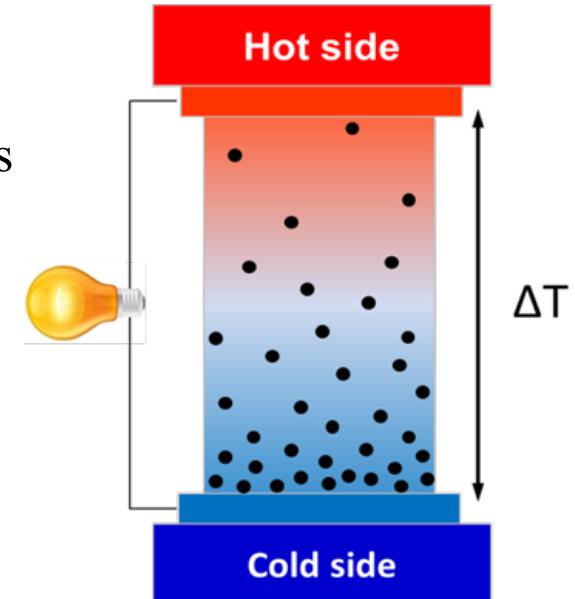
Thermoelectric Field E

Thermogalvanic cells

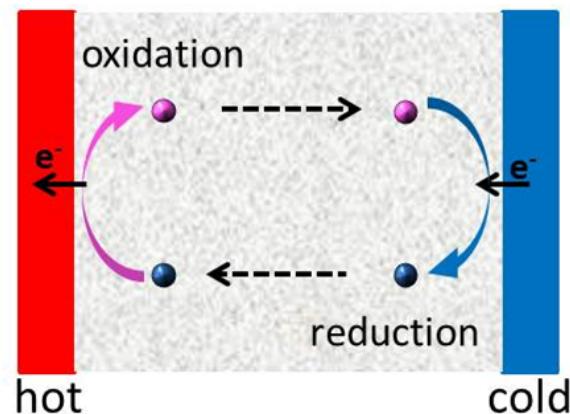
THERMOGALVANIC CELLS

- contains a liquid electrolyte and a redox couple
- temperature dependent electrode potential is termed as “Seebeck potential”.

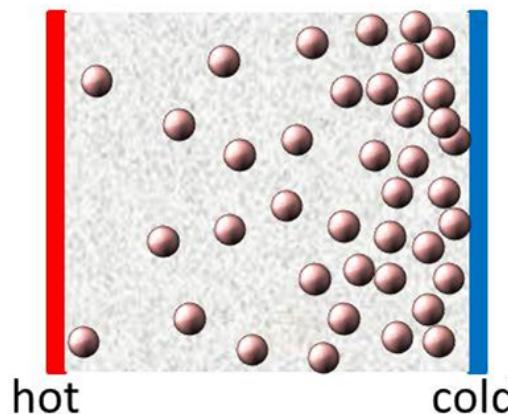
$$S_e = - \frac{\Delta V}{\Delta T}$$



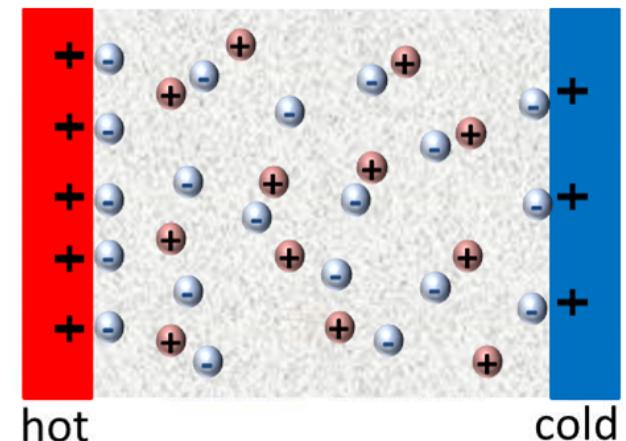
a) Thermogalvanic (redox)



b) Thermodiffusion



c) Electronic double layer



THERMOGALVANIC EFFECT

If the redox reaction in the liquid electrolyte containing very small ions is



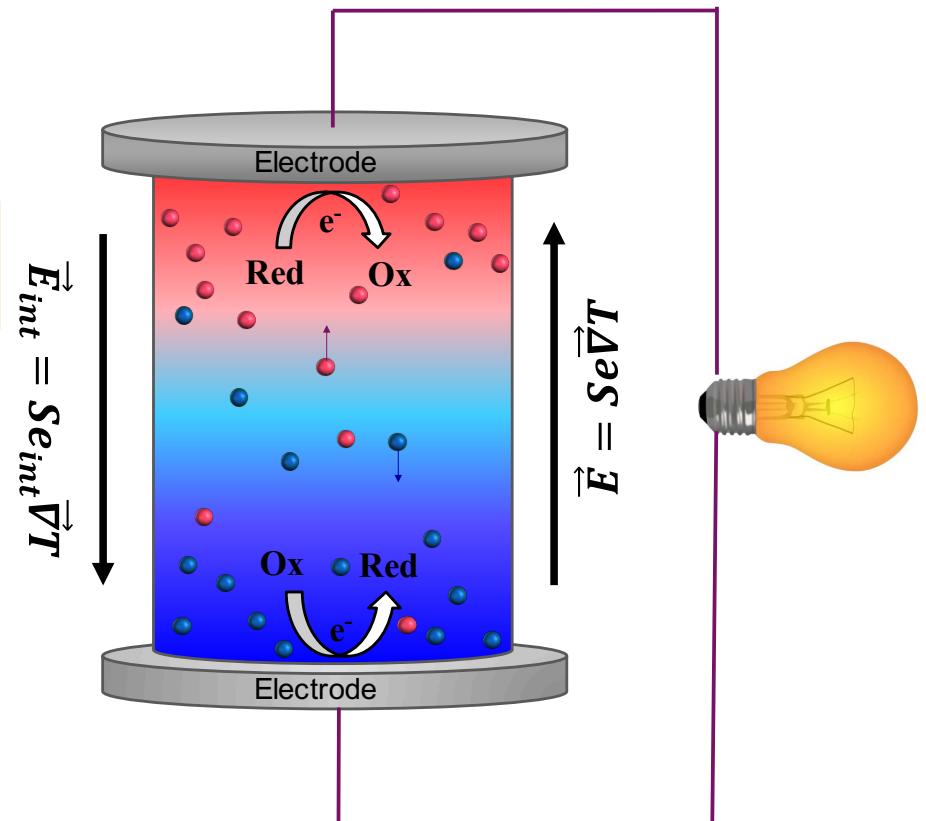
the Seebeck coefficient S_e is given by

$$S_e = \left(\frac{dE}{dT} \right)_{t \rightarrow \infty} = \frac{1}{nF} [(S_B + \hat{S}_B) - (S_A + \hat{S}_A) - n\bar{s}]$$

where, S_A and S_B are the partial molar entropies of A & B and \hat{S}_A & \hat{S}_B are their Eastman entropies. \bar{s} is the transported energy of the electrons in the circuit.

$$S_e = \left(\frac{dE}{dT} \right)_{t \rightarrow \infty} = \frac{(S_B - S_A)}{nF} = - \frac{\Delta s_{rc}}{e}$$

as in most of the electrolytes, \hat{S}_A & \hat{S}_B are too small; \bar{s} being the order of $\mu\text{V/K}$, and thus can be neglected.



THERMODIFFUSION EFFECT

In complex electrolytes containing macroscopic ions, colloidal particles etc. at the onset of ΔT there arises a particle current given by,

$$\vec{J}_{N_i} = -D_i \left[\vec{\nabla} n_i + n_i \frac{\hat{S}_i}{k_B T} \vec{\nabla} T - n_i \frac{\xi_i e}{k_B T} \vec{E} \right]$$

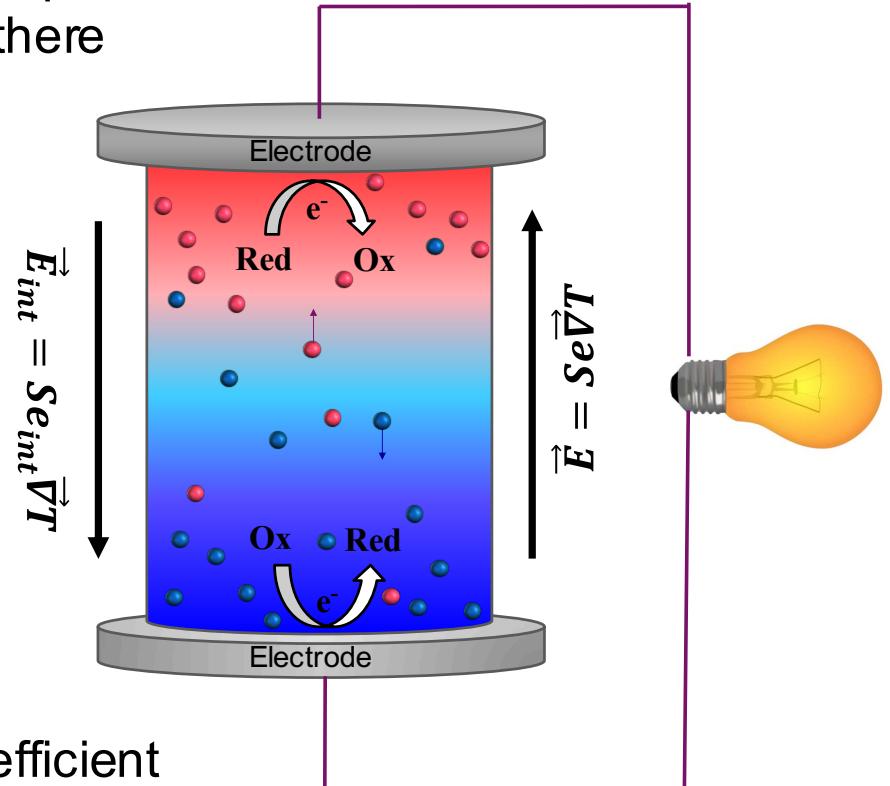
This particle current gives rise to an internal electrical field \vec{E}_{int} within the bulk,

$$\vec{E}_{int} = S e_{int} \vec{\nabla} T; \Delta V_{int} = -S e_{int} \Delta T$$

$S e_{int}$ is the corresponding internal Seebeck coefficient

** \vec{E}_{int} difficult to measure experimentally but can be inferred from the Soret coefficient, S_T

$$S_T = \frac{\hat{S}_i}{k_B T} - \frac{\xi_i e}{k_B T} S e_{int}^{Eq}$$



The redox half reaction occurring at the electrode is given by,

$$\sum_j v_j A_j + e^- = 0$$

where, v_j is the stoichiometric coefficient and A_j the chemical formula of the species j

At local thermodynamic equilibrium condition,

$$\sum_j v_j \tilde{\mu}_j + \tilde{\mu}_e = 0$$

where, $\tilde{\mu}_j = \mu_j + z_j eV^i$
and $\tilde{\mu}_e = \mu_e - eV^{elect}$

μ_j and $\tilde{\mu}_j$ represents the electrochemical and chemical potential of the species j.

The potential difference between two electrodes held at different temperatures can be written as:

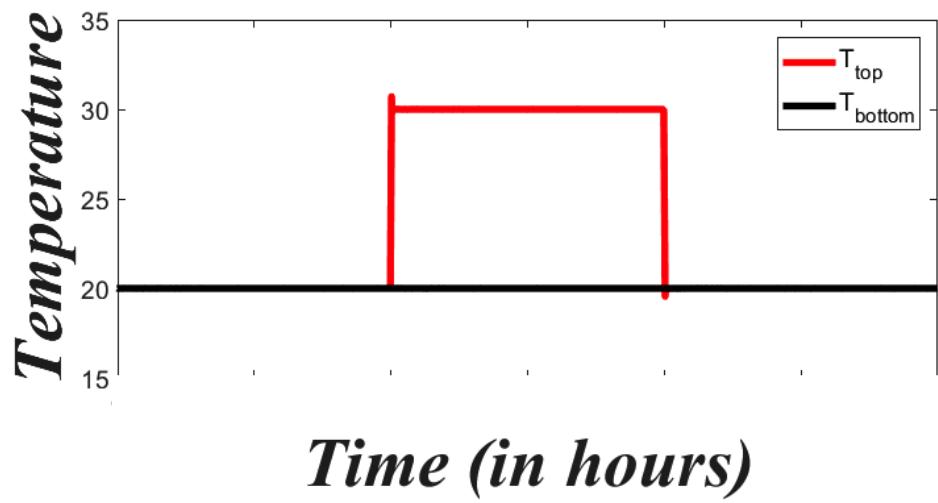
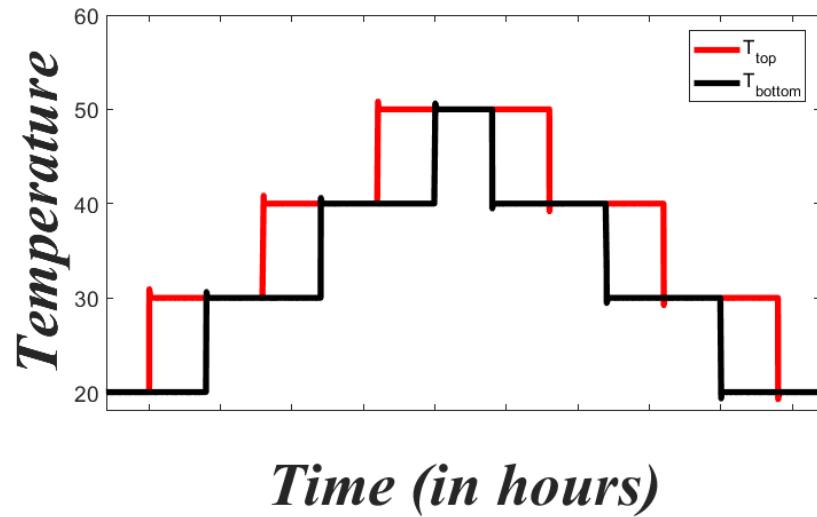
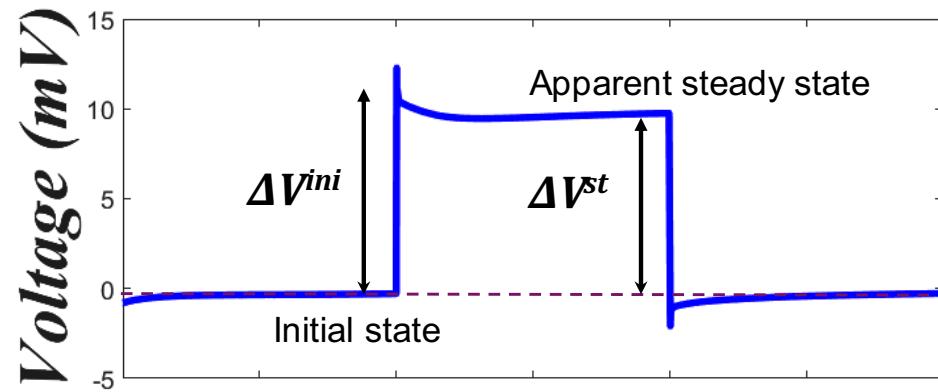
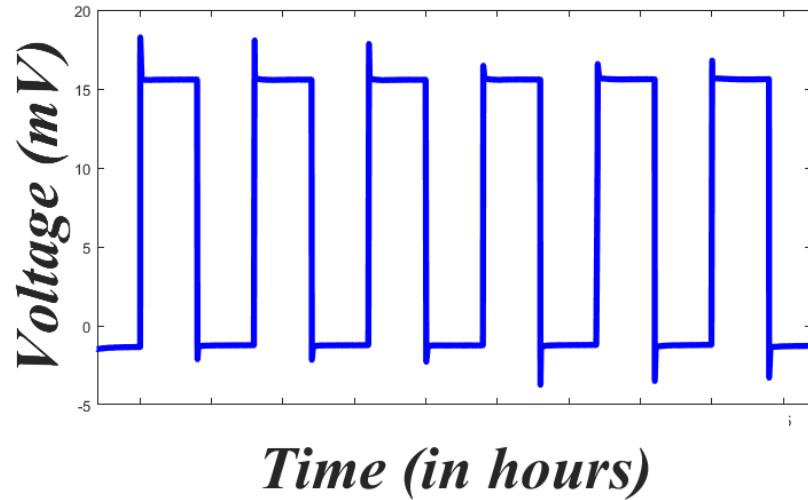
$$e\Delta V^{elect} = \sum_j v_j (\Delta\mu_j + z_j e\Delta V_{int}) + \Delta\mu_{e-}$$

$$= \Delta \sum_j v_j \mu_j - e \cdot Se_{int} \cdot \Delta T + \Delta\mu_{e-}$$

$$\Delta_r G = \sum_j v_j \mu_j,$$

$$Se_{measured} = -\frac{\Delta V^{elect}}{\Delta T} = -\frac{\Delta \sum_j v_j \mu_j}{e} + Se_{int}$$

WHAT WE MEASURE



At the onset of ΔT , when the concentration of all species is still homogeneous

$$\vec{\nabla} n_i \rightarrow 0$$

So, the particle current becomes,

$$\vec{J}_{N_i} = -D_i \left[n_i \frac{\hat{S}_i}{k_B T} \vec{\nabla} T - n_i \frac{\xi_i e}{k_B T} \vec{E}_{int}^{ini} \right]$$

As we are in open circuit, the total electric current is zero i.e. $\sum_i z_i e \vec{J}_{N_i} = 0$

Rearranging the current equation we get,

$$\vec{E}_{int}^{ini} = \frac{\sum_i z_i e n_i D_i^* \hat{S}_i}{\sum_i z_i e^2 n_i D_i^* \xi_i} \vec{\nabla} T = \left[\sum_i t_i \frac{\hat{S}_i}{\xi_i e} \right] \vec{\nabla} T \quad \left| \begin{array}{l} t_i = \frac{z_i \xi_i e^2 n_i D_i^*}{\sum_i z_i \xi_i e^2 n_i D_i^*} = \frac{\sigma_i}{\sigma_{tot}} \\ \text{is the Hittorf number} \end{array} \right.$$

$$Se_{int}^{ini} = \sum_i t_i \frac{\hat{S}_i}{\xi_i e}$$

The combined initial Seebeck coefficient is, therefore,

$$Se^{ini} = Se_{int}^{ini} - \frac{\Delta \sum_j v_j \mu_j}{e} = \frac{1}{e} \left(-\Delta S_{rc} + \sum_i t_i \frac{\hat{S}_i}{\xi_i} \right)$$

STATIONARY STATE: SORET EQUILIBRIUM

Sufficient time after the temperature gradient has been applied,

$$\vec{J}_{N_i} = 0$$

The particle flux equation becomes,

$$\vec{J}_{N_i} = -D_i \left[\vec{\nabla} n_i + n_i \frac{\hat{S}_i}{k_B T} \vec{\nabla} T - n_i \frac{\xi_i e}{k_B T} \vec{E}_{int}^{Eq} \right] = 0$$

$$\vec{E}_{int}^{Eq} = \frac{\sum_i z_i n_i \hat{S}_i}{e \cdot \sum_i z_i n_i \xi_i} \vec{\nabla} T$$

$$Se_{int}^{Eq} = \frac{\sum_i z_i n_i \hat{S}_i}{e \cdot \sum_i z_i n_i \xi_i}$$

As all particle current ceases, $\Delta\mu_j = z_j e \cdot Se_{int}^{Eq} \Delta T - \bar{S}_j \Delta T$, $\Delta \sum_j v_j \mu_j = \left[Se_{int}^{Eq} - \frac{1}{e} (\sum_j v_j \bar{S}_j) \right] e \Delta T$

The combined initial Seebeck coefficient is, therefore,

$$Se^{Eq} = Se_{int}^{Eq} - \frac{\Delta \sum_j v_j \mu_j}{e} = Se_{int}^{Eq} - Se_{int}^{Eq} - \frac{1}{e} \left(\sum_j v_j \bar{S}_j \right) = \frac{1}{e} \left(\sum_j v_j \bar{S}_j \right) = \frac{1}{e} \left(\sum_j v_j S_j + v_j \hat{S}_j \right)$$

$$Se^{Eq} = \frac{1}{e} \left(-\Delta s_{rc} + \sum_j v_j \hat{S}_j \right)$$

STATIONARY STATE SEEBECK COEFFICIENT AND SORET COEFFICIENT

Ludwig-Soret coefficient S_T is given by

$$\frac{\vec{\nabla} n}{n} = -S_T \vec{\nabla} T$$

The particle current at stationary state

$$\vec{\nabla} n_i + \left(n_i \frac{\hat{S}_i}{k_B T} - n_i \frac{\xi_i e}{k_B T} Se_{int}^{Eq} \right) \vec{\nabla} T = 0$$

Rearranging the above equation we get,

$$\frac{\vec{\nabla} n}{n} = - \left(\frac{\hat{S}_i}{k_B T} - \frac{\xi_i e}{k_B T} Se_{int}^{Eq} \right) \vec{\nabla} T$$

This gives us the direct relationship between the Se_{int}^{Eq} and the Ludwig-Soret coefficient, S_T

$$S_T = \frac{\hat{S}_i}{k_B T} - \frac{\xi_i e}{k_B T} Se_{int}^{Eq}$$

Ferrofluids for thermoelectric materials

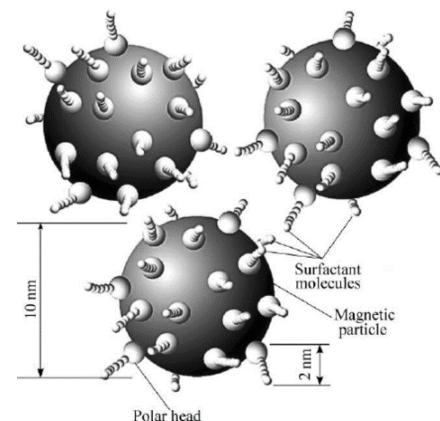
A ferrofluid (FF) is a colloidal suspension of single-domain magnetic particles, dispersed in a liquid carrier**.



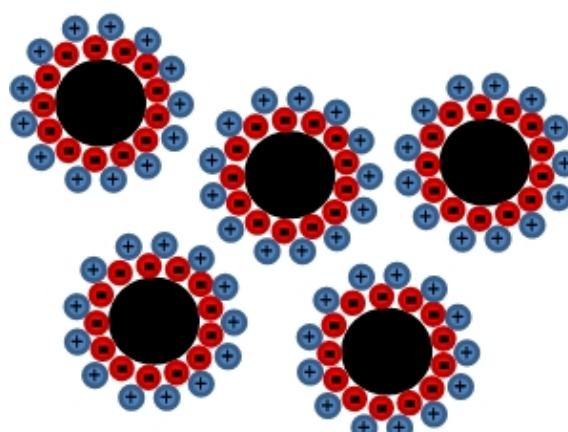
\hat{S} ↑ Thermoelectric coefficient ↑
 Thermodiffusion coefficient ↑

Two different classes of ferrofluids:

Surfacted ferrofluids**



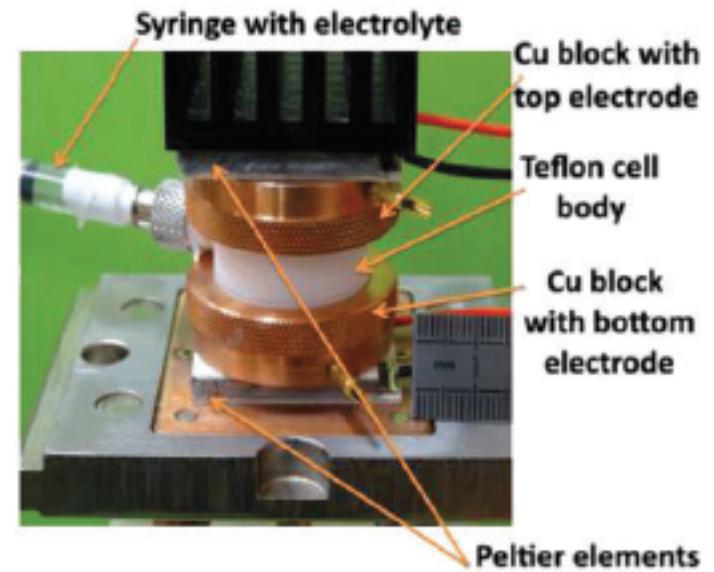
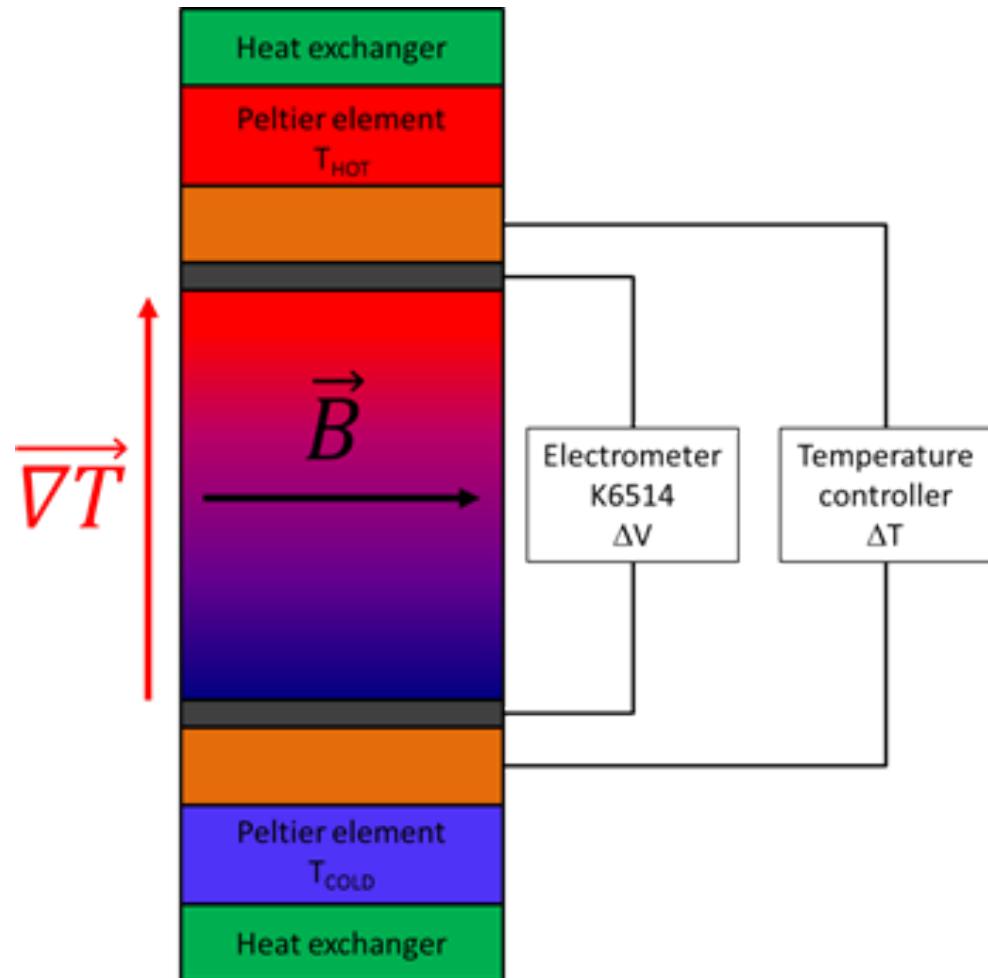
Ionic ferrofluids



**C. Scherer et al./Brazilian Journal of Physics, 35, 2005

**S. A. Novopashin/Thermophysics and Aeromechanics, 2015, 22

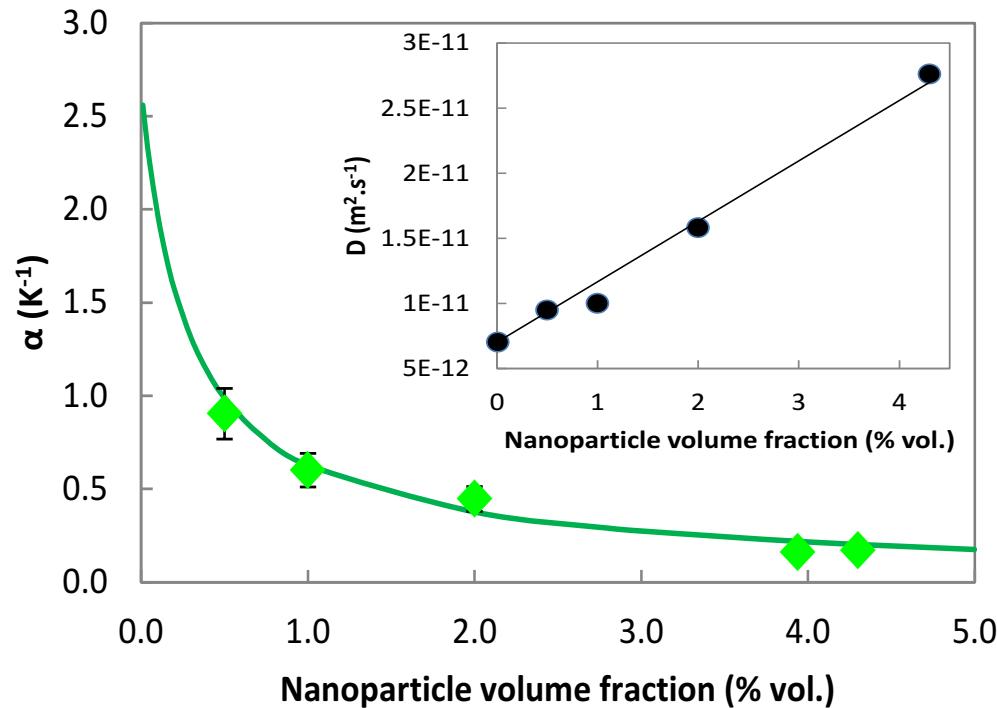
THERMOELECTRIC EXPERIMENTAL SETUP



- $V = 600 \mu\text{l}$
- $d_{\text{electrodes}} = 10 \text{ mm}$

$$S_e = - \frac{\Delta V}{\Delta T}$$

DMSO BASED FERROFLUIDS



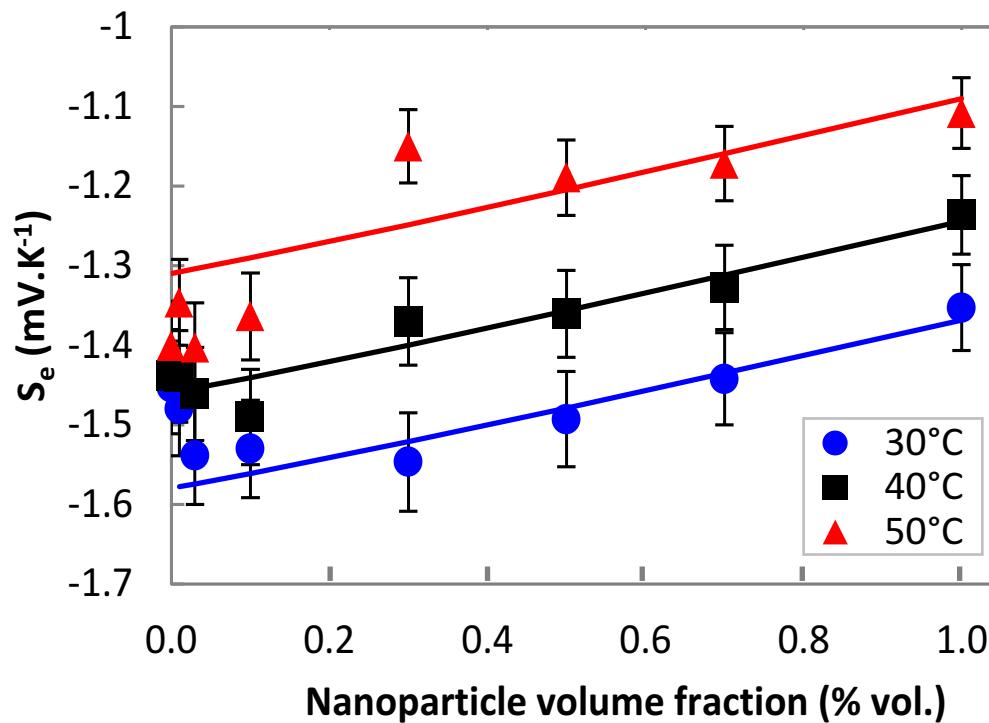
Measured at laboratory PHENIX (Paris, France)
using Forced Rayleigh Scattering

$$\hat{S}_0 = 68 \pm 8 \text{ meV.K}^{-1}$$



$\gamma\text{-Fe}_2\text{O}_3$ ($d_{NP}=6.7 \text{ nm}$)
DMSO (Seebeck effect negligible)
Fc/Fc+ redox couple

$$S_T = \frac{\hat{S}_i}{k_B T} - \frac{\xi_i e}{k_B T} S e_{int}^{Eq}$$



Se_{ini} as a function of nanoparticle volume fraction (φ), at different temperatures

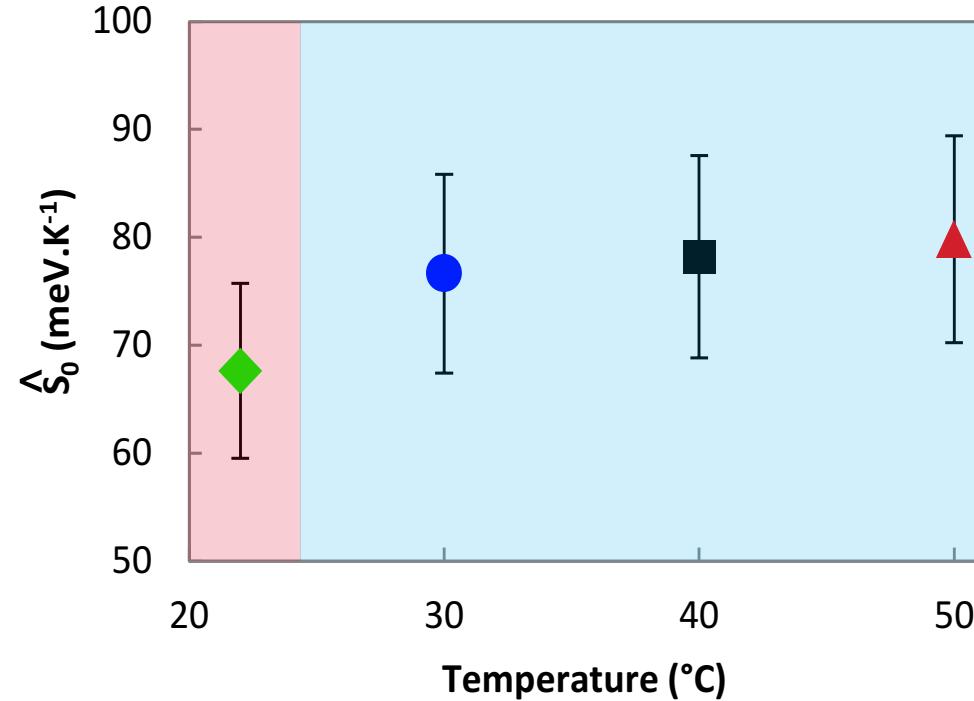
As we know,

$$Se_{ini} = \frac{1}{e} \left(-\Delta_r S + \sum_i t_i \frac{\hat{S}_i}{\xi_i} \right)$$

Concentration of Redox couples was always kept same.

$$Se^{ini}(\varphi) - Se^{ini}(0) = \frac{t_{NP}(\varphi) \hat{S}_{NP}}{e \cdot \xi_{NP}} \\ = \frac{\xi_i e n_i D_i}{\sigma_T} \hat{S}_{NP}(\varphi)$$

Where, χ =osmotic compressibility
 ξ_i = effective charge of the NPs
 φ = NP volume concentration
 n_i = total no. of nanoparticles
 \hat{S} = Eastman entropy of transfer
 σ_T = Total conductivity



$\widehat{S}_0 \sim 75 \text{ meV.K}^{-1} >> 0.12 \text{ meV.K}^{-1}$ for Na^+ in water

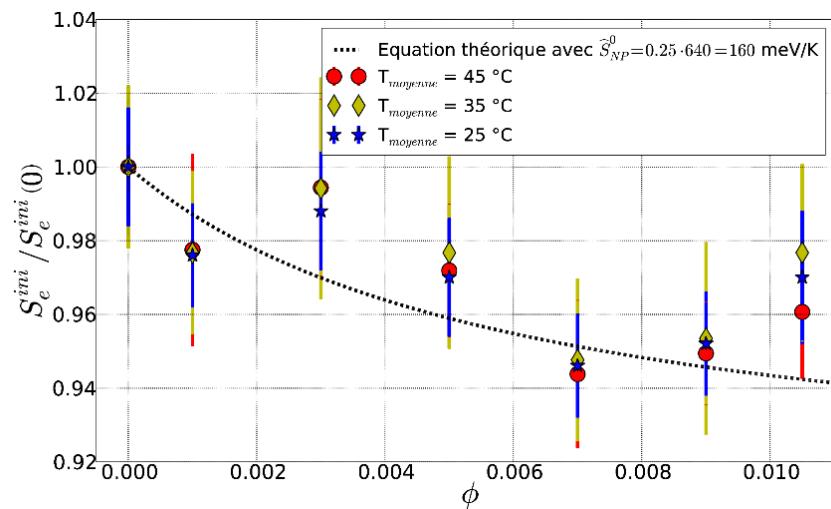
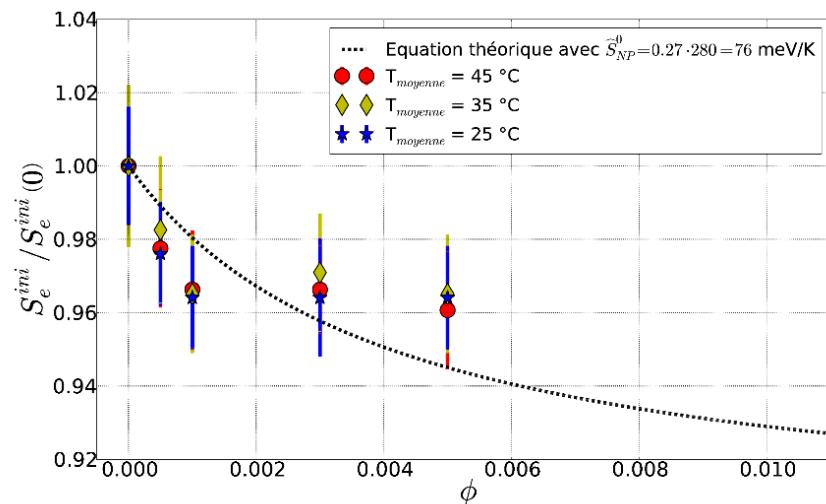
- Initial state Se measurements corroborates with the Forced Rayleigh Scattering measurements

AQUEOUS FERROFLUIDS FOR THERMOELECTRIC MATERIALS

3mM $\text{Fe}(\text{CN})_6^{3-}$
& $\text{Fe}(\text{CN})_6^{4-}$

Physical characteristics of FF-SSC and FF-Y1SC

Ferrofluid	d_0 (nm)	Φ_{max} (%)	D ($\times 10^{-11} \text{ m}^2/\text{s}$)	ξ^0	$\xi^0/S (\text{nm}^{-2})$
FF-SSC	7,2	0,54	1,80	-280	-1,7
FF-Y1SC	11,9	1,13	1.18	-640	-1,5

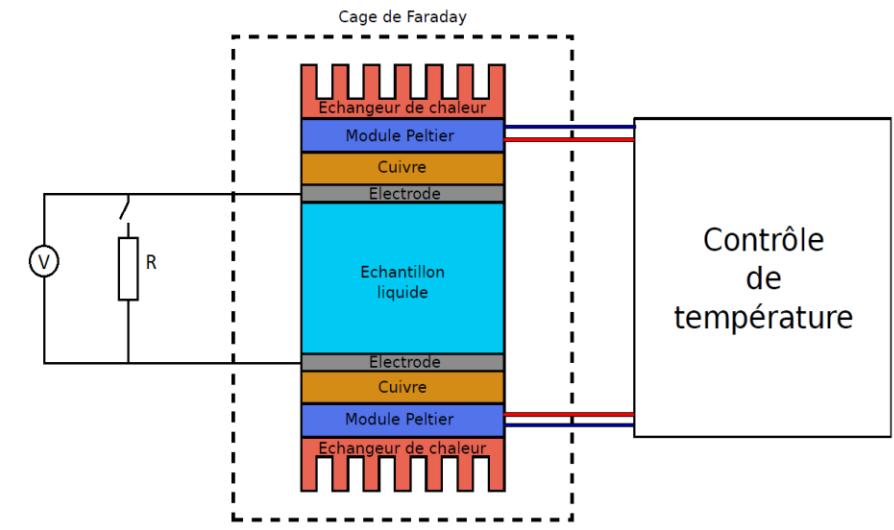
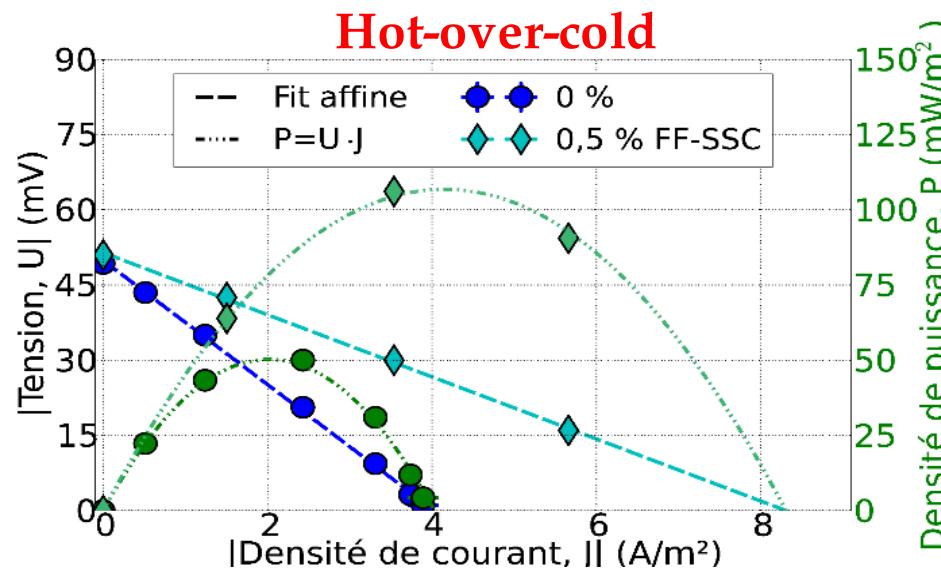


$$\Delta S_e = S_e^{ini}(\phi) - S_e^{ini}(0) = \frac{t_{NP}(\phi)\hat{S}_{NP}}{e \cdot \xi_{NP}} = \frac{\xi_i e \varphi D_i}{\sigma_T} \frac{\xi_i e n_i D_i}{\sigma_T} \hat{S}_{NP}(\phi)$$

$$\begin{aligned}\hat{S}_{SSC}^0 &= 76 \pm 17 \text{ meV/K} \\ \hat{S}_{Y1SC}^0 &= 160 \pm 32 \text{ meV/K}\end{aligned}$$

** S_e^{ini} decreased with the addition of NP concentration

AQUEOUS FERROFLUIDS FOR THERMOELECTRIC MATERIALS



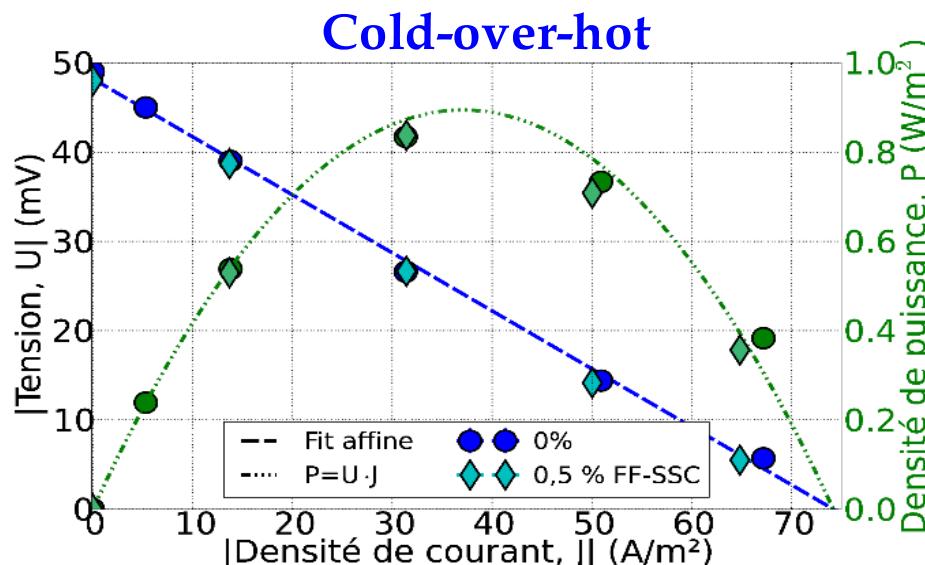
@ hot-over-cold configuration

$$\begin{aligned} P_{\max} (\phi_{\text{SSC}}=0\%) &= 50 \text{ mW/m}^2 \\ P_{\max} (\phi_{\text{SSC}}=0,5\%) &= 100 \text{ mW/m}^2 \end{aligned}$$

And @ cold-over-hot configuration is:

$$P_{\max} (\phi_{\text{SSC}}=0,5\%) = 900 \text{ mW/m}^2$$

- ✓ Power output augments with the addition of NPs in FF-SSC.
- ✓ Convection diminishes the resistance of transport of matter.





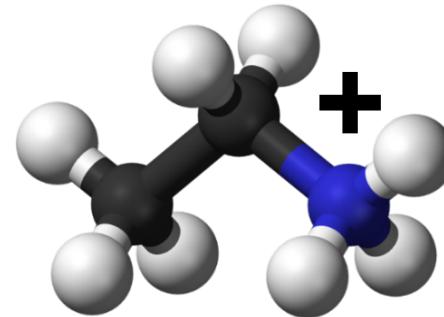
Ionic liquid based ferrofluids as thermoelectric materials

Why ionic Liquids?

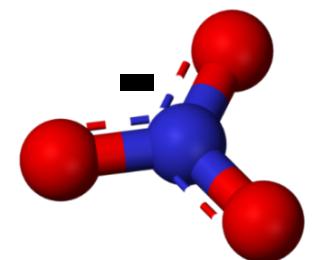
- High thermal stability and high electrochemical stability
- Ability to dissolve wide range of metal-salts and organic compounds
- High intrinsic ion conductivity and lower thermal conductivity
- Strong electrostatic interactions which render them non-volatile and therefore of low flammability.

Ethyl Ammonium Nitrate

- Ionic liquid with a melting point at 12 °C and a boiling point at 240 °C
- Electric conductivity of 20 mS.cm^{-1} , 10^5 times larger than pure water
- Thermal conductivity of $0.26 \text{ W.m}^{-1}.K^{-1}$, twice as much as water
- High thermogalvanic coefficient of redox couple iodine/iodide
- pH scale between 0 and 10



Ethylammonium cation



Nitrate anion

IONIC LIQUID BASED FERROFLUIDS AS THERMOELECTRIC MATERIALS



EAN-FF($\phi=1\%$)

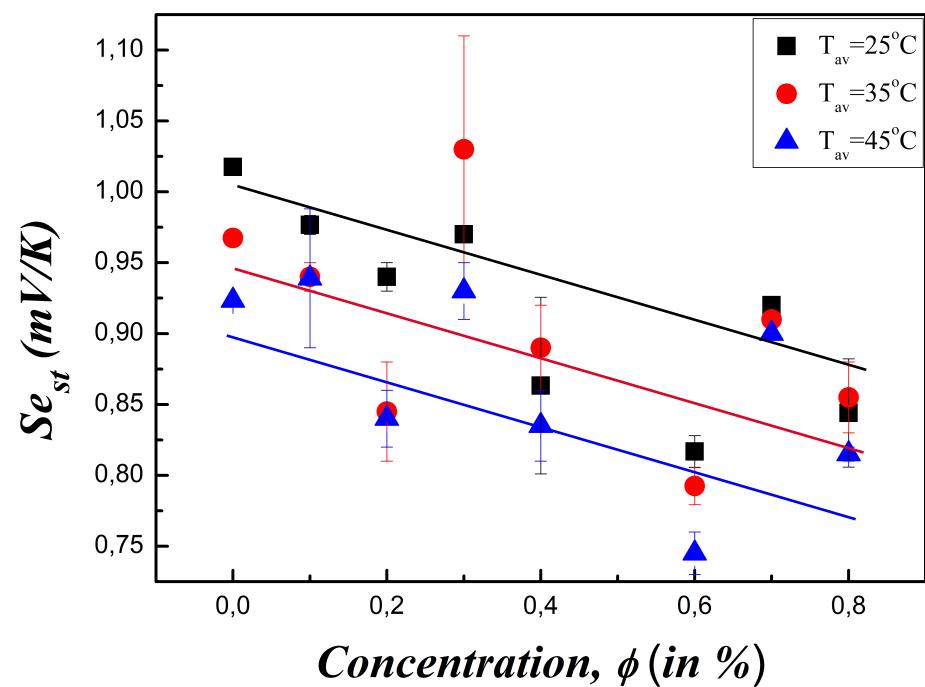
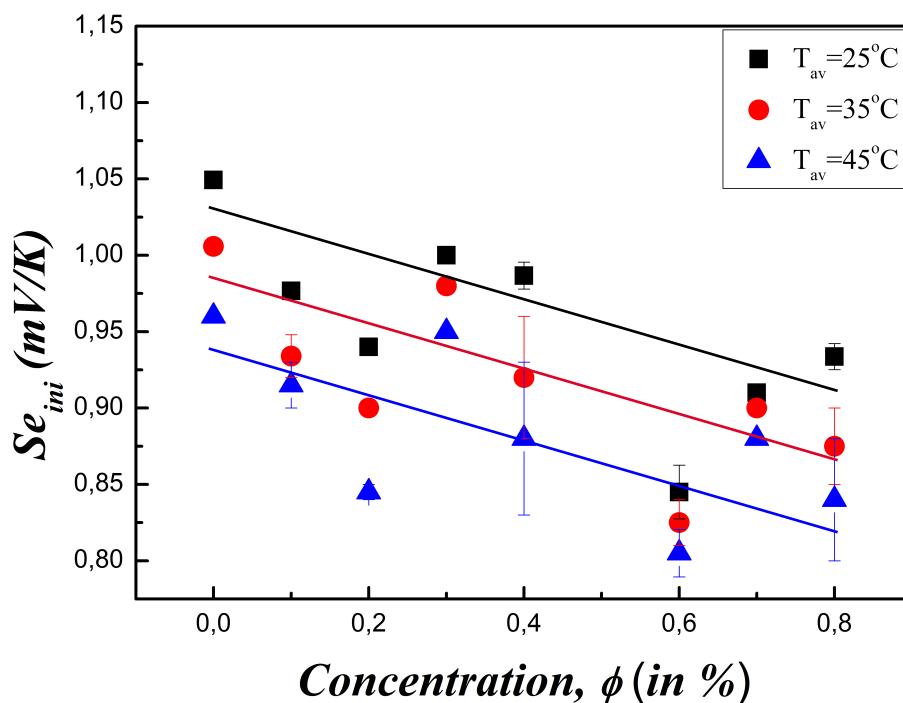
Nanoparticles: $\gamma\text{-Fe}_2\text{O}_3$ ($d_{NP}=7.34\text{ nm}$)

Redox couple : I_2/I^-

Solvent : EAN

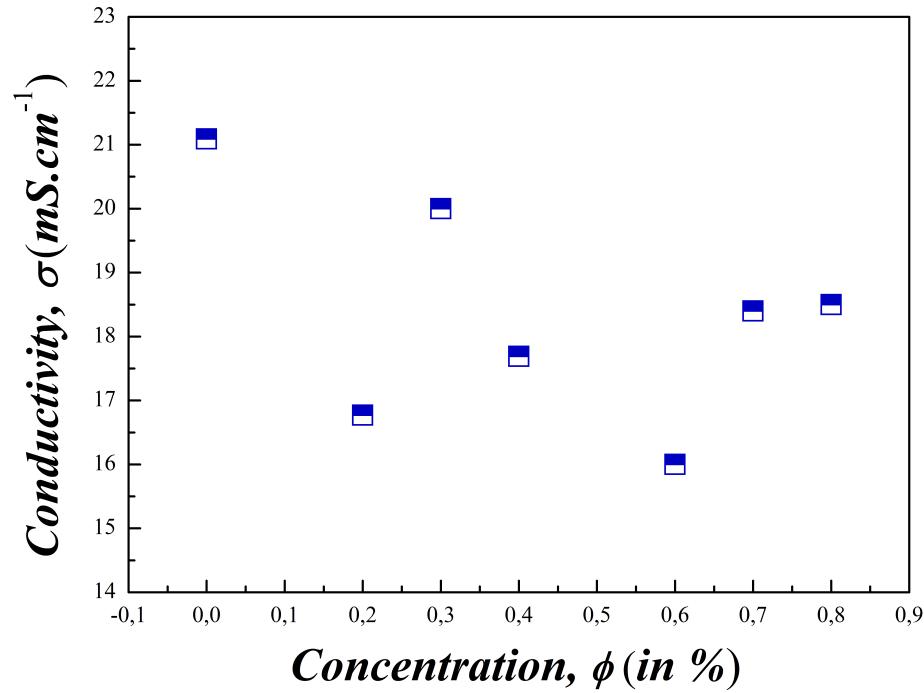
Counter ion : Citrate ions

Redox reaction at the electrodes

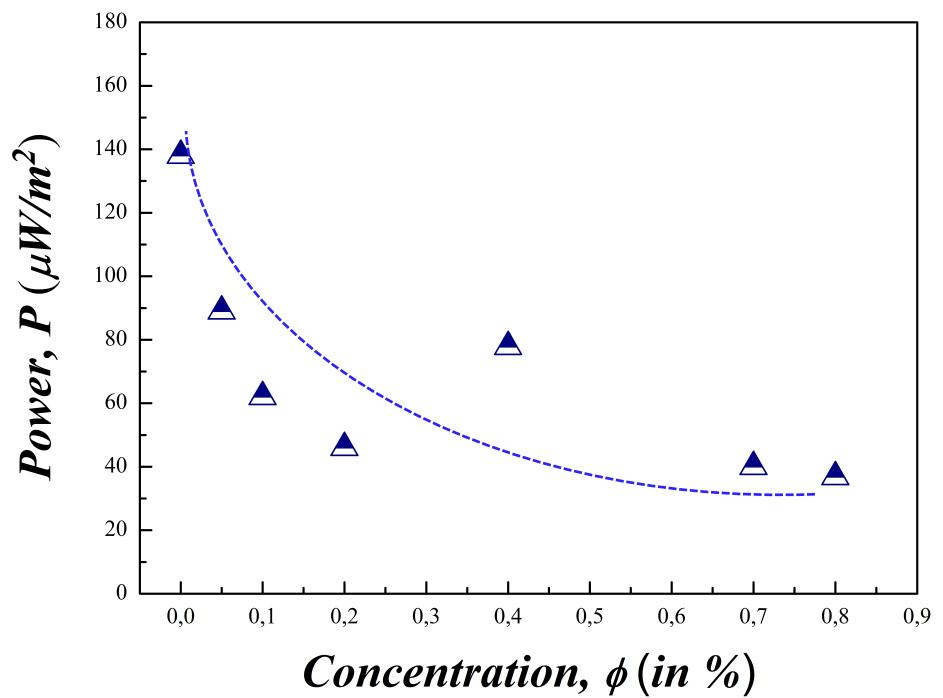


** Se_{ini} and Se_{st} decreases with increase in NP concentration

IONIC LIQUID BASED FERROFLUIDS AS THERMOELECTRIC MATERIALS



Conductivity as a function of FF concentration



Power measurements for EAN-FF at different ϕ

IONIC LIQUID BASED FERROFLUIDS AS THERMOELECTRIC MATERIALS

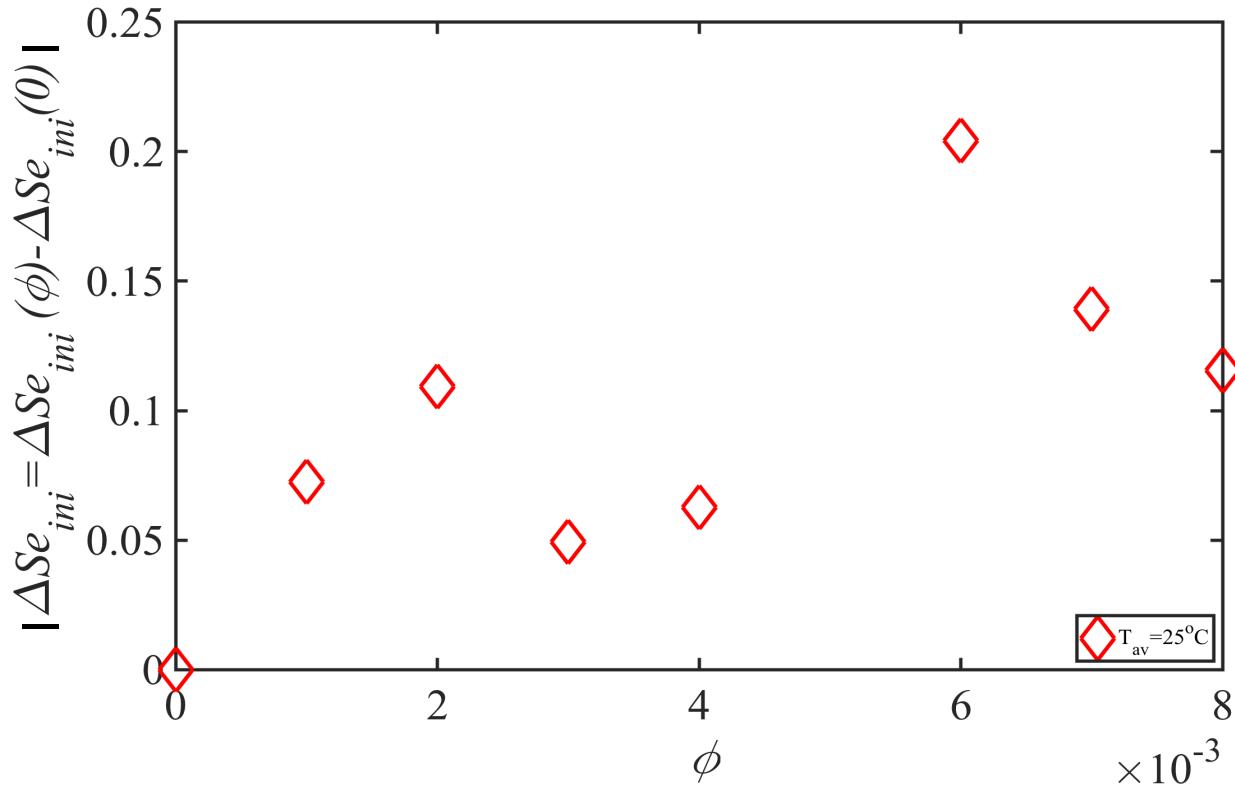
$$\Delta Se = Se^{ini}(\varphi) - Se^{ini}(0) = \frac{t_{NP}(\varphi)\hat{S}_{NP}}{e \cdot \xi_{NP}} = \frac{\xi_i e n_i D_i}{\sigma_T} \frac{\xi_i e n_i D_i}{\sigma_T} \hat{S}_{NP}(\varphi)$$

For EAN-FF, we know

$$D_i = 1.34 \times 10^{-12} \text{ m}^2/\text{s}$$

$$\xi = -60$$

$$d = 7.4 \text{ nm}$$



From Seebeck

$$\frac{\hat{S}_0}{k_B T} = 700 K^{-1}$$

From FRS

$$\frac{\hat{S}_0}{k_B T} = 8 K^{-1}$$

Another surface effect??

or

Wrong model??

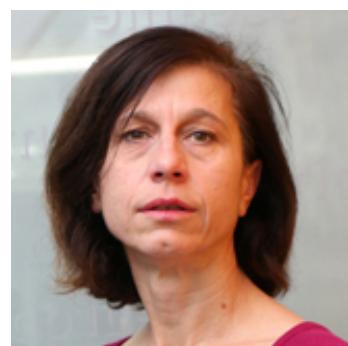
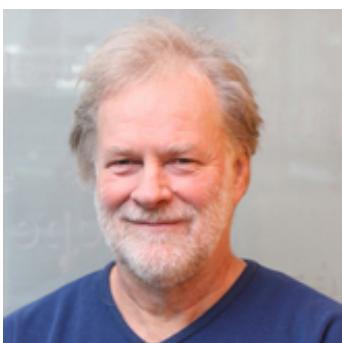
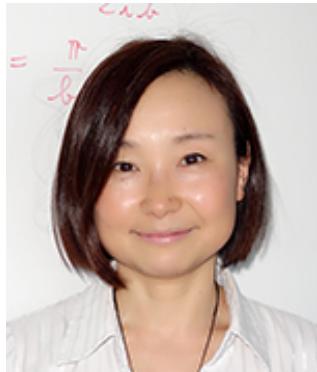
Summary and Perspectives

SUMMARY AND PERSPECTIVES

- Seebeck coefficient in ferrofluid based electrolytes decreases with the increase in NP concentration.
- Augmented power output with increase in aqueous ferrofluid concentration due to forced convection.
- First thermoelectric measurements in ionic liquid based ferrofluids.
- Many physical parameters are unknown in ionic liquids for correct analysis.
- Maybe another physical effect on the electrode surface in complex ionic liquid based electrolytes
- The theoretical model for weak electrolytes may not be suitable for complex electrolytes such as ionic liquids

ACKNOWLEDGEMENT

This work is supported by European Union's Horizon 2020 research and innovation programme under the grant agreement No 731976 (MAGENTA)



Thank you for your attention!!

Commissariat à l'énergie atomique et aux énergies alternatives

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hYdrodynamique, éNergie et complexité

THEORETICAL CONSIDERATIONS

The volume fraction ϕ dependence on the nanoparticles' \hat{S} and ξ in eqn (1) can be inferred from a hard-sphere model. In the Carnahan-Starling equation** of state for a hard-sphere gas, the isothermal osmotic compressibility is given by:

$$\chi(\phi_{\text{eff}}) = \frac{(1 - \phi_{\text{eff}})^4}{1 + 4\phi_{\text{eff}} + 4\phi_{\text{eff}}^2 - 4\phi_{\text{eff}}^3 + \phi_{\text{eff}}^4}$$

where, the effective volume fraction $\phi_{\text{eff}} = \varphi(d_{\text{eff}}/d)^3$, with an effective core diameter $d_{\text{eff}} = d + 2\lambda_D$ where λ_D is the screening length.

$$\xi = \xi_0 \chi(\phi_{\text{eff}}) \text{ and } \hat{S} = \hat{S}_0 \chi(\phi_{\text{eff}})$$

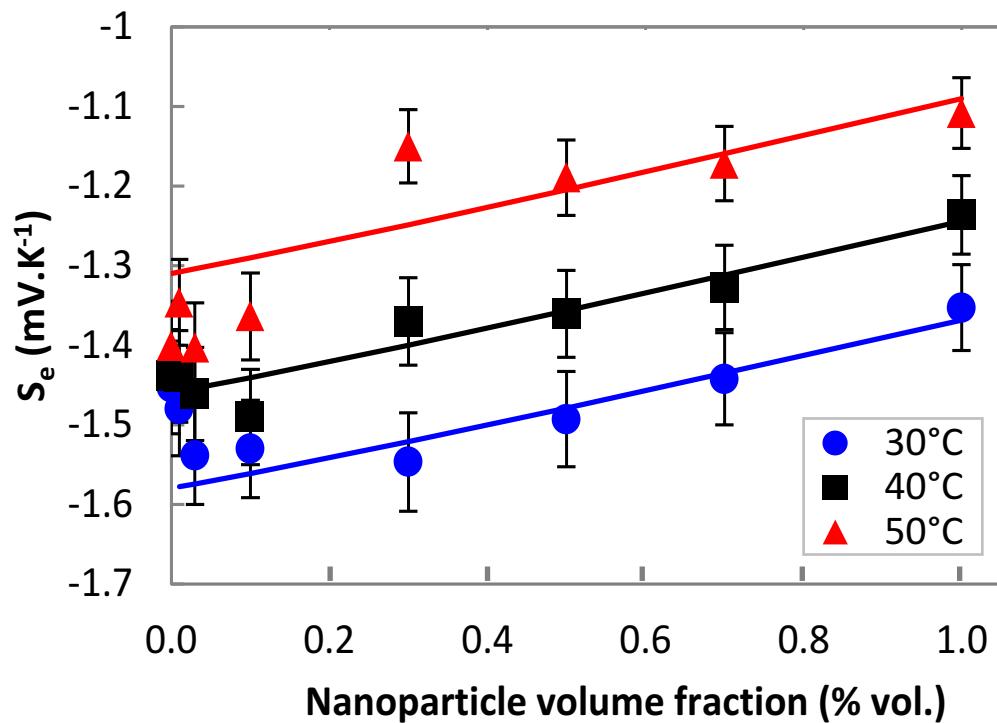
where, ξ_0 and \hat{S}_0 are defined as the limit $\phi \rightarrow 0$ of ξ and \hat{S} respectively.

Eqn (1) can be simplified as;

$$\Delta S_e = S_e^{ini}(\varphi) - S_e^{ini}(0) = \frac{t_{NP}(\varphi)\hat{S}_{NP}^0}{e \cdot \xi_{NP}^0} = \frac{\xi_i e \varphi n_i D_i}{\sigma_T} \hat{S}_{NP}^0 \chi(\varphi)$$

where t_i is the Hithorf transport number, corresponding to the relative contributions of ionic conductivities σ_i to the total conductivity σ_T and is represented as:

$$t_i = \frac{\sigma_i}{\sum \sigma_i} = \frac{z_i \xi_i e^2 n_i D_i}{\sum_i z_i \xi_i e^2 n_i D_i} \quad \text{where } D_i \text{ is the diffusion coefficient}$$



Se_{ini} as a function of nanoparticle volume fraction (φ), at different temperatures

As we know,

$$Se_{ini} = \frac{1}{e} \left(-\Delta_r S + \sum_i t_i \frac{\hat{S}_i}{\xi_i} \right)$$

Concentration of Redox couples was always kept same.

$$Se_{ini}(\varphi) - Se_{ini}(0) = \frac{1}{e} \sum_i t_{NP} \frac{\hat{S}_{NP}}{\xi_{NP}}$$

$$\Rightarrow \Delta Se_{ini} = \frac{Ze\varphi}{V_{NP}} \frac{D(\varphi)}{\sigma_T} \hat{S}(\varphi_{eff})$$

Where, D =Diffusion coefficient

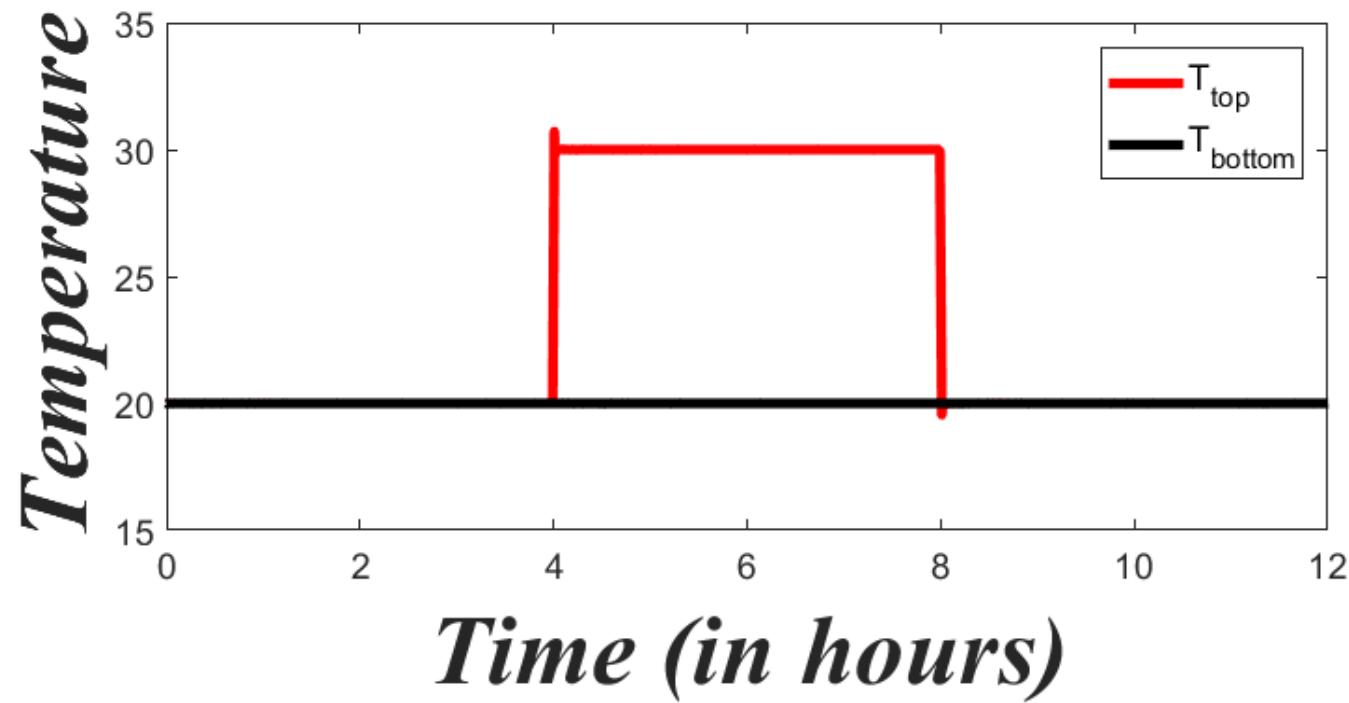
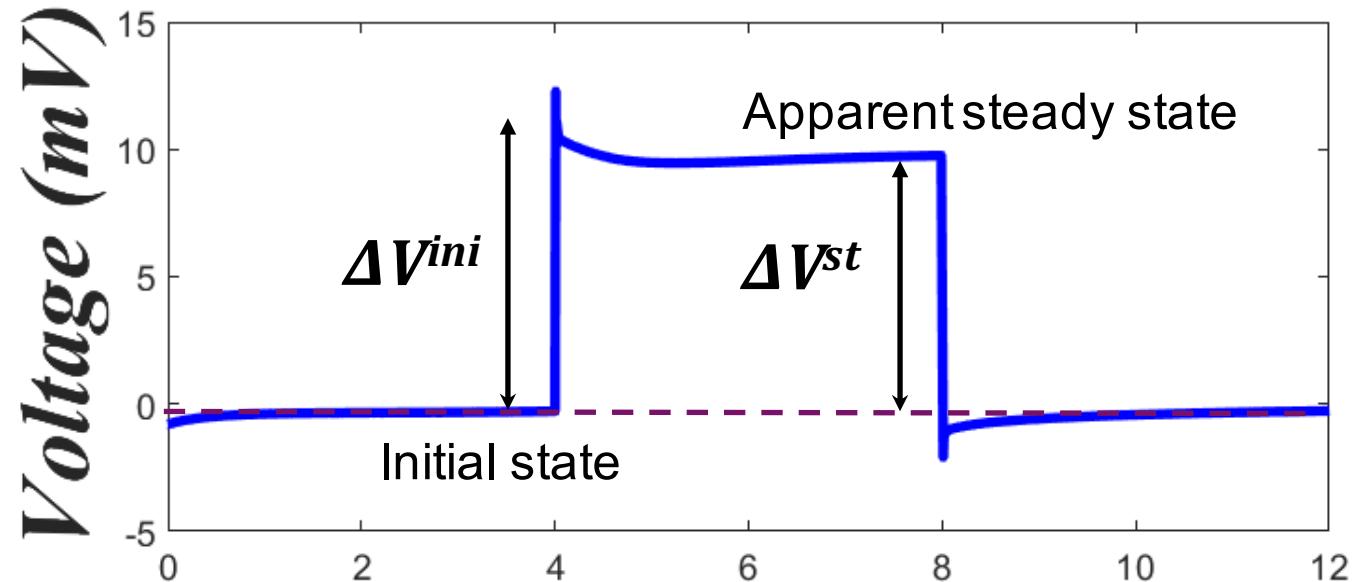
Z = effective charge of the NPs

φ = NP volume concentration

V_{NP} = volume of a nanoparticle

\hat{S} = Eastman entropy of transfer

σ_T = Total conductivity



THEORETICAL CONSIDERATIONS

Eqn (1) can be rewritten as;

$$\Delta Se = Se^{ini}(\phi) - Se^{ini}(0) = \frac{t_{NP}(\phi)\hat{S}_{NP}^0}{e \cdot \xi_{NP}^0} = \frac{\xi_i e \phi D_i}{\sigma_T} \hat{S}_{NP}^0 \chi(\phi_{eff})$$

where, t_{NP} = Hitthorff transport number, and is represented as: $t_{NP} = \frac{\sigma_{NP}}{\sigma_T}$

σ_{NP} = ionic conductivity of the nanoparticles

σ_T = total ionic conductivity of the electrolyte

$\chi(\phi_{eff})$ = isothermal osmotic compressibility from the hard sphère model

D_i = diffusion coefficient of the NPs

ϕ_{eff} = effective volume fraction of the NPs

\hat{S}_{NP}^0 = Eastman entropy of transfer of the NPs at infinite dilution

STATIONARY STATE: SORET EQUILIBRIUM

Sufficient time after the temperature gradient has been applied,

$$\vec{J}_{N_i} = 0$$

The particle flux equation becomes,

$$\begin{aligned} \vec{J}_{N_i} &= -D_i \left[\vec{v} n_i + n_i \frac{\hat{S}_i}{k_B T} \vec{v} T - n_i \frac{\xi_i e}{k_B T} \vec{E}_{int}^{Eq} \right] = 0 \\ \sum_i z_i \vec{v} n_i + \sum_i z_i n_i \frac{\hat{S}_i}{k_B T} \vec{v} T - \sum_i z_i n_i \frac{\xi_i e}{k_B T} \vec{E}_{int}^{Eq} &= 0 \quad \text{Can dissappear} \\ \sum_i z_i n_i \frac{\hat{S}_i}{k_B T} \vec{v} T &= \sum_i z_i n_i \frac{\xi_i e}{k_B T} \vec{E}_{int}^{Eq} \quad \left| \quad \sum_i z_i \vec{v} n_i = \vec{v} \left(\sum_i z_i n_i \right) = 0 \right. \\ \vec{E}_{int}^{Eq} &= \frac{\sum_i z_i n_i \hat{S}_i}{e \cdot \sum_i z_i n_i \xi_i} \vec{v} T \\ Se_{int}^{Eq} &= \frac{\sum_i z_i n_i \hat{S}_i}{e \cdot \sum_i z_i n_i \xi_i} \end{aligned}$$

As all particle current ceases, $\Delta\mu_j = z_j e \cdot Se_{int}^{Eq} \Delta T - \bar{S}_j \Delta T$. So, $\Delta_r G = \sum_j v_j \mu_j = [Se_{int}^{Eq} - \frac{1}{e} (\sum_j v_j \bar{S}_j)] e \Delta T$

The combined initial Seebeck coefficient is, therefore,

$$Se^{Eq} = Se_{int}^{Eq} - Se_{int}^{Eq} - \frac{1}{e} \left(\sum_j v_j \bar{S}_j \right) = \frac{1}{e} \left(\sum_j v_j \bar{S}_j \right) = \frac{1}{e} \left(\sum_j v_j S_j + v_j \hat{S}_j \right)$$

$$Se^{Eq} = \frac{1}{e} \left(-\Delta_r S + \sum_j v_j \hat{S}_j \right)$$

INTERNAL SEEBECK FIELD

The redox half reaction occurring at the electrode is given by,

$$\sum_j v_j A_j + e^- = 0$$

where, v_j is the stoichiometric coefficient and A_j the chemical formula of the species j and e represents one electron.

At local thermodynamic equilibrium condition,

$$\sum_j v_j \tilde{\mu}_j + \tilde{\mu}_e = 0$$

where, $\tilde{\mu}_j = \mu_j + z_j e V^i$
and $\tilde{\mu}_e = \mu_e - e V^{elect}$

μ_j and $\tilde{\mu}_j$ represents the electrochemical and chemical potential of the species j . V^i the internal potential of the solution near the electrode and V^{elect} the potential inside the conducting electrode.

The potential difference between two electrodes held at different temperatures can be written as:

$$e\Delta V^{elect} = \sum_j v_j (\Delta\mu_j + z_j e\Delta V^i) + \Delta\mu_{e^-}$$

$$= \Delta\Delta_r G - e \cdot Se_{int} \cdot \Delta T + \Delta\mu_{e^-}$$

$$Se = -\frac{\Delta V^{elect}}{\Delta T} = -\frac{(\Delta\Delta_r G + \Delta\mu_{e^-})}{e \cdot \Delta T} + Se_{int}$$

$\Delta\Delta_r G = \sum_j v_j \mu_j$, is the Gibbs free energy of the redox couples

$$Se = Se_{int} - \frac{\Delta\Delta_r G}{e \cdot \Delta T}$$

$$= \Delta\Delta_r G + \Delta V^i \cdot e \sum_j (v_j \mu_j) + \Delta\mu_e -$$

THERMOELECTRICITY IN COMPLEX FLUIDS

