

Thermodiffusion of ions in nanoconfined aqueous electrolytes

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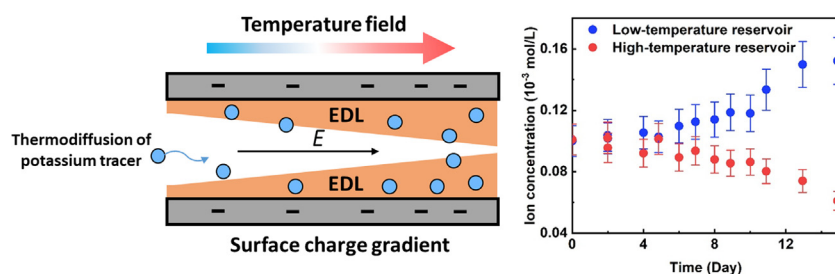
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GRAPHICAL ABSTRACT

Synopsis: thermodiffusion in nanoporous media is an important fundamental process in many environmental and technical applications from desalination to nuclear waste storage.



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ABSTRACT

Understanding of thermal effects on ion transport in porous media is very important for environmental applications. The movement of ions along a temperature gradient is named thermophoresis or thermodiffusion. In nanoporous media, where the interaction of ions with solid–liquid interfaces has a significant influence on their migration, the theoretical understanding of thermodiffusion is still incomplete. Herein, we present experimental results for the thermodiffusion of cations in saturated nanoporous silica by the through-diffusion method. Both the experimental data and theoretical analysis indicate that the temperature-induced polarization of surface charges strongly influences ionic transport. Stated simply, the electric field in a liquid electrolyte confined in nanopores changes when the applied temperature gradients are altered, thereby affecting the motion of the nanoconfined ionic species. By applying an external temperature field, the gradient of the surface charge density leads to the charged aqueous species exhibiting strong temperature gradient-dependent electrophoretic mobility. When the thickness of the electrical double layer is comparable to the size of the nanopores, the theory used herein indicates that this kind of nonisothermal ionic mobility is up to one order of magnitude larger than classical thermophoretic mobility. This study improves the understanding of the underlying mechanisms that govern the transport of ions in nanoporous media, which could set the stage for diffusional metamaterials induced by specific thermal fields.

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1. Introduction

The Soret effect describes the motion of particles along a temperature gradient ∇T , also called thermophoresis or thermodiffusion. Thermodiffusion and its relevant effects have been investigated for a long time due to its relation to important applications, for example, the migration of radionuclides and other contaminants, cell physiology and energy conversion [1–4]. For a simple diluted electrolyte, the linear relationship between the thermodiffusive flux J_T and the temperature gradient ∇T is assumed to be $D_T C = J_T / \nabla T$, with the proportion coefficient D_T as the thermodiffusion coefficient and an ion concentration C . By comparing to the ionic diffusivity in free water D_0 , the Soret coefficient S_T is defined as the ratio $S_T = D_T / D_0$, which characterizes the magnitude of thermodiffusion; it is positive when an ion moves to the cold side of a system and negative when the ion moves to the hot side of a system. While a variety of investigations have promoted microscopic explanations of the Soret effect in a bulk system during the past few years [1,5,6], relatively few studies extend to confined systems such as nanoporous media.

Comparing to the bulk ones, the properties of the solid–liquid interface have more significant impacts on the physical and chemical characteristics of local electrolytes in a nanoconfined space, which further influences the transport of ionic species [7,8]. Therefore, if the physicochemical properties of the solid–liquid interface are sensitive to temperature [9–11], species transport in nanopores might also be strongly responsive to an external temperature gradient. The electrical double layer (EDL) is a structure on a charged surface, which is caused by the electrostatic interaction of ions with a surface and the thermal motion of ions. Its effect (the so-called electrokinetic effect) is one of the most important interfacial properties [12]. Previous studies indicated that the structure of the EDL is highly depended on the surrounding temperature [13,14]. For instance, the surface reactivity of a solid, the permittivity of a confined electrolyte and the self-diffusion of ions related to the EDL are all strongly sensitive to the local temperature. Furthermore, a completely or partially overlapping EDL within nanopores might magnify the influence of temperature on the transport of nanoconfined ions [15,16]. Several studies have already addressed isothermal ionic transport in nanoporous media at various temperatures [17,18], yet the microscopic understanding of nonisothermal ionic transport in nanoporous media has remained unclear, especially from an experimental perspective.

In this work, we use the transport of potassium ions in a nanoscale membrane as an experimental system to address the above question. The diffusion of potassium tracers is implemented in nanoporous silica membranes (NPSMs) saturated with a NaCl electrolyte and various moderate temperature gradients are used along the transport direction. The experimental data show an abnormal inversion of the Soret coefficient of the confined potassium tracers, which is consistent with our proposed electrochemical model. We analytically and computationally show ion fluxes as a function of various thermal conditions and EDL thicknesses to address the significant role of an overlapping EDL on ion transport at the nanoscale with different thermal gradients. These findings can also provide a critical and robust mechanism to manipulate contaminant transport and separation. In summary, this study unveils the remarkable roles of temperature as a controller that regulates the electrochemical properties of an interface and the transport of nanoconfined ions.

2. Materials and methods

2.1. Preparation of the nanoporous silica membrane (NPSM)

The NPSM is fabricated with sintered SiO₂ nanoparticles. Nano-sized SiO₂ powder (particle size: 15 ± 5 nm, purity: $\geq 99.8\%$, SSA: 250 ± 30 m²/g) was purchased from Zhongkehang, China. To decrease the viscosity of the concentrated nanoparticles, the nano-sized SiO₂ powder was mixed with ultrapure water at a mass ratio of 1:9. The thick paste was then heated in an oven at 373 K for 24 h to remove moisture. Polyvinyl alcohol (PVA, purity: $\geq 99.0\%$, source: aladdin) was completely dissolved in ultrapure water to get 3 wt% polyvinyl alcohol solution. Afterward, 1.38 g of the treated SiO₂ powder was fully blended with 0.2 mL of the dissolved polyvinyl alcohol solution, ground and sifted through a 100-mesh stainless steel sieve, then pressed in a cylindrical mold for 2 min (2–4 MPa). The nanosized SiO₂ sheet had a diameter of 3.1 cm and a thickness of 3.2 mm. It was later heated in a furnace at 1073 K in an air atmosphere to form a compact solid (NPSM). Morphological characterization of the NPSM was carried out by using scanning electron microscopy (GeminiSEM 500, Zeiss, China). The pore size distribution and specific surface area were measured using mercury intrusion porosimetry (Autopore IV 9510, Micromeritics, USA) and a nitrogen adsorption analyzer (Tristar II 3020, Micromeritics, USA). Fig. 1-A shows a typical scanning electron microscopy image of this porous silica at the nanoscale, which has a mean pore size \bar{d} of 10–20 nm (Fig. S1-C).

2.2. Fabrication of the through-diffusion cell

The through-diffusion cell is a sandwich structure, and the NPSM is located at the middle layer, each side of which tightly bonds double-decker sheet-like microchambers. Fig. 1-B illustrates the cross-section of this sandwich structure. The two outer metallic microchambers are stuck in the inner metallic plates. The cooled/heated ultrapure water at constant temperature, produced by a refrigerating machine and hot water bath kettle, quickly flows inside the outer microchambers to maintain their temperatures and create a steady thermal gradient inside the NPSM. Temperature sensors are attached to the outer metallic chambers to continuously monitor the real-time temperature variation. Two inner microchambers are the column-shaped flow channels carved inside the inner metallic plates and separated by the NPSM. The NPSM is embedded in a hollow polymethyl methacrylate (PMMA) plate and fixed by thermally insulated glue. Silicone pads are placed between the plates to avoid water leakage. The inner microchambers are partially open, and therefore, the electrolyte inside the inner microchambers can enter the NPSM. In addition, the inner microchambers are also connected with the outer reservoirs to create an electrolyte loop between the inner microchambers and outer reservoirs by a peristaltic pump. In this way, a mixed solution of sodium chloride (NaCl) and potassium iodide (KI) is pumped into each inner chamber and circulated (a detailed schematic is shown in Fig. S1-D). Herein, the background aqueous solution NaCl is used to maintain a steady ionic strength. Furthermore, the tracer concentration has to be significantly lower than the NaCl concentration to avoid an interference on the local ionic strength. Potassium is chosen as tracer because its surface selectivity coefficient or binding energy sequence on silica surfaces is close to the of one of sodium [19,20]. The flux of the potassium tracers through the NPSM is monitored by analyzing their concentration

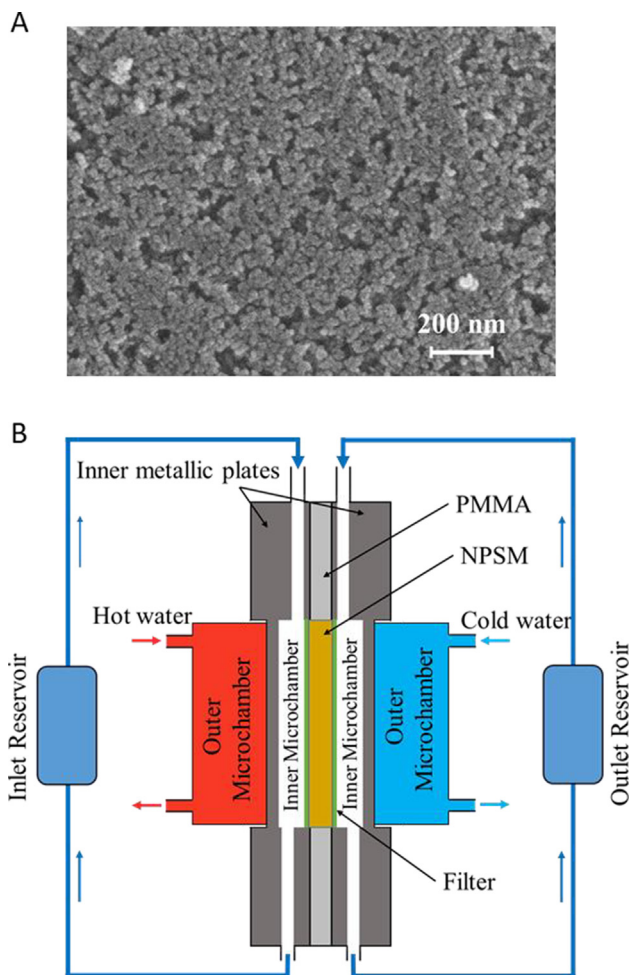


Fig. 1. Schematics of the NPSM and the through-diffusion cell. (A) Typical SEM image of the tested NPSM and (B) schematic cross-section of the through-diffusion cell, which combines the NPSM (two photographs of the NPSM with millimeter- and micrometer-level resolutions are shown in Fig. S1) with two double-decker sheet-like microchambers.

over time in the outer reservoirs on both sides; this method has been described in previous publications [21,22].

3. Results and discussion

3.1. Diffusion of ions under isothermal conditions

The inner microchambers are first connected to the two outer reservoirs with a 1.0 mM NaCl solution to presaturate the NPSM. After a presaturation period of one week, the reservoirs are replaced. A new reservoir (inlet reservoir) containing 500 mL of 1.0 mM NaCl with a given tracer concentration (0.1 mM KI) is then connected to the inner microchamber on one side of the NPSM. The inner microchamber on the other side is connected to a new reservoir (outlet reservoir) containing 80 mL of 1.0 mM NaCl. Initially, the diffusion experiment is carried out at room temperature (298 K) to elaborate on the isothermal diffusion of ions in nanoporous media. Due to the difference in the tracer concentration between the two sides of the NPSM, the KI tracer diffuses into the low concentration reservoir; therefore, the concentration of the KI tracer increases over time. The low concentration reservoir is monitored at one-day intervals, and the ion concentration is analyzed by ion chromatography (ICS1000/2000, Dionex, USA). In Fig. 2-A, the points show the evolution of the tracer concentration

over time in the low-concentration reservoir, where the potassium concentration increases much more drastically to reach a steady state compared with that of iodide. This is much different from KI transport in micrometer pores, where the electroneutrality is maintained in pore solution, thereby resulting in the same trend for both potassium and iodide ions [23]. Note that the silica surface is negatively charged when immersed in the given pore solution [24]. Therefore, the strong electrostatic interaction of the negatively charged surface with the nanoconfined ions can promote the diffusion of cations but inhibit that of anions within the nanopores of the NPSM, where electroneutrality is not present [25].

3.2. Diffusion of ions under nonisothermal conditions

After elaboration of the classical pattern for the isothermal diffusion of ions in nanoscale porous media, through-diffusion experiments under nonisothermal conditions were performed by using temperature gradients of 10, 20 and 30 K across the diffusion cell. After the same presaturation as in the isothermal experiments, the inner microchambers on both sides were connected to a new reservoir containing a NaCl solution (1 mM or 10 mM) mixed with 0.1 mM KI tracer. Here, we implement different temperature gradients on the NPSM by controlling the temperature at $T_{in} = 313$ K, 318 K and 323 K in the outer microchamber, while the temperature at the outlet is adjusted to $T_{out} = 303$ K, 298 K and 293 K, respectively; thus, the average temperature is maintained at $\bar{T} = 308$ K. Accounting for the temperature drop across the filters on both sides, the actual temperature difference across the NPSM is $\Delta T = 0.914(T_{out} - T_{in}) = 9.1$ K, 18.3 K, 27.4 K, respectively. The ionic Soret coefficient in the bulk solution becomes larger with decreasing salt concentration or increasing average temperature [5,26]. For the given average temperature (308 K) and potassium tracer concentration (0.1 mM), previous experimental and theoretical studies [26,27] indicated that the Soret coefficient of ions in bulk systems is positive and on the order of $\sim 10^{-3} \text{ K}^{-1}$, which implies that the ions are thermophobic and move toward the cold region. However, as exemplarily shown in Fig. 2-B, with a temperature gradient of 18.3 K and nanoconfinement, the potassium tracers exhibit opposite behavior compared to the bulk solution and move toward the high-temperature side.

3.3. Thermal-electrochemical coupling mechanism

To reveal the mechanisms of this unexpected thermodiffusion of nanoconfined potassium ions in the NPSM, we employ a coupled thermal electrochemical (CTE) model to analyze the different contributions to the ion flux. In the present system, with \bar{u}_T being the thermoosmotically average velocity within nanopores in the NPSM, the Péclet number is negligibly small $Pe = \bar{u}_T \bar{d} / D_0 \ll 1$ (see Appendix for details), indicating that compared with ionic diffusion, the ionic motion driven by thermoosmosis can be ignored. By simplifying a porous structure that includes pores and a solid matrix into a simple homogeneous medium, the effective diffusivity $D_{i,e}$ reflects the case in which the i^{th} species demonstrates Fickian diffusion in this simple medium. The value of $D_{i,e}$ relates to the corresponding diffusivity in free water $D_{i,0}$ by a structure factor G as $D_{i,e} = D_{i,0}/G$ [28]. By treating the ions as point charges, the ion flux \mathbf{J}_i can be described as [29–31]:

$$\mathbf{J}_i = -D_{i,e} \nabla C_i - D_{i,e} z_i C_i \nabla \psi^* - D_{i,e} S_T C_i \nabla T \quad (1)$$

with an ionic valence z_i and a dimensionless electric potential $\psi^* = F\psi/RT$. In the above equation, F and R are the Faraday constant and ideal gas constant, respectively. The first two terms on the right-hand side of Eq. (1) account for Fickian diffusion and electrophoresis, given by the Nernst-Planck equation. The last term is

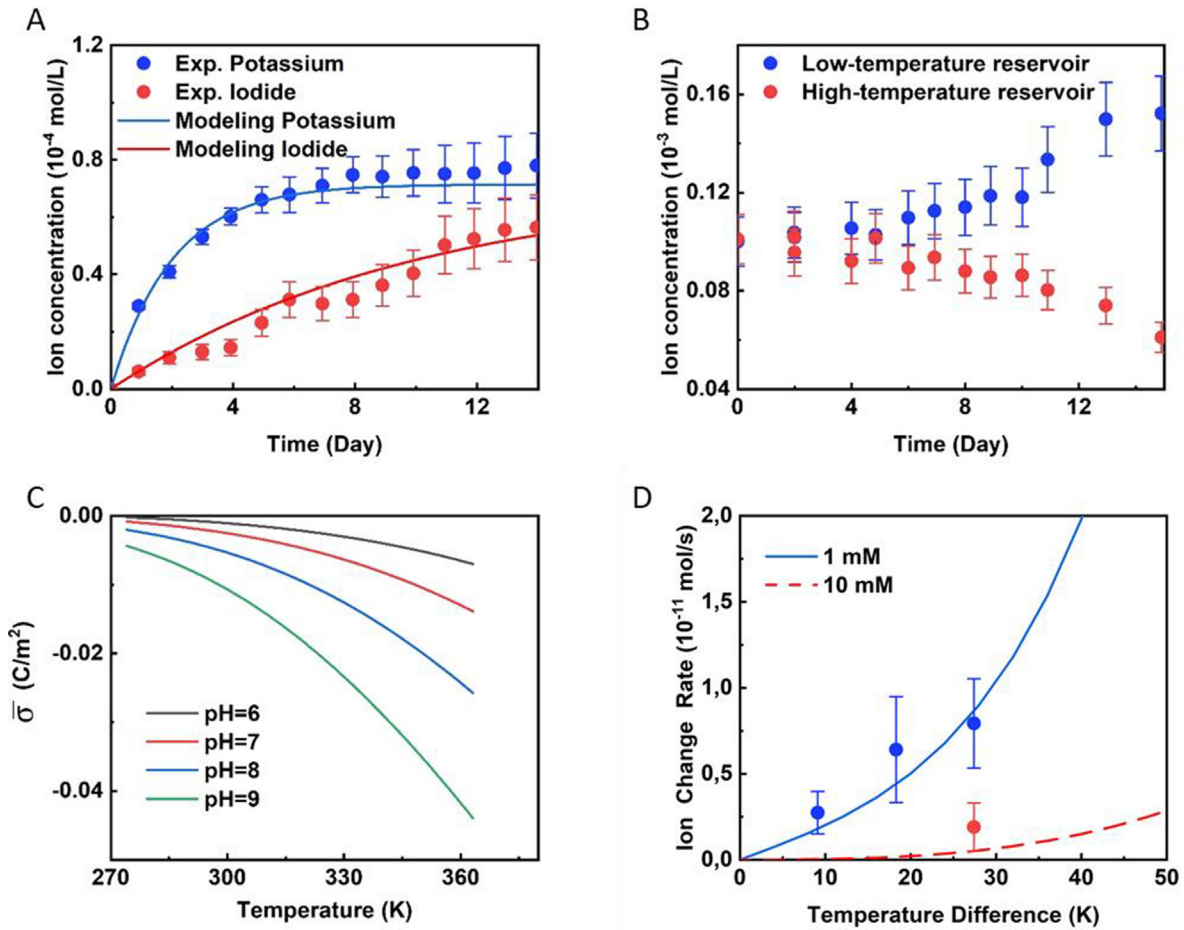


Fig. 2. Experimental and modeling results in nanoconfined aqueous electrolytes. (A) Measured (squares) and modeled (lines) concentrations of potassium and iodide ions in the outlet reservoirs under isothermal conditions at room temperature. (B) Potassium concentrations in the reservoirs on both sides after applying a $\Delta T = 18.3$ K temperature difference. The background solution is 1 mM NaCl. (C) Effective surface charge density $\bar{\sigma}$ of the NPSM as a function of pH and temperature according to the temperature-dependent charge regulation model described in the Appendix ($C_0^r = 1$ mM). (D) Mean change rates δC of potassium ions in the outer reservoirs with different temperature differences ΔT in 1 mM and 10 mM NaCl electrolytes. The squares are the measured data, while the lines are calculated by our CTE (coupled thermal electrochemical) model.

used to calculate the thermodiffusive flux. Regarding a simple symmetric pore solution in charged porous media and using the Donnan theory together with the local charge balance of the pore solution with a solid surface, one finds the dimensionless local concentration of potassium ions [32,33]:

$$C_i^* = C_i/C_{i,b}^r = z_i \rho / 2 + \sqrt{(\rho / 2)^2 + 1} \quad (2)$$

with the dimensionless volume charge density $\rho = -Q/FC_0^r$. In the above equation, the superscript “r” refers to the corresponding term in the reservoir, $C_{i,b}^r$ and C_0^r are the concentrations of the tracer and the sum of cation concentrations, respectively, and Q is the charge density per volume carried by the solid matrix of the NPSM, which is calculated by $Q = \bar{\sigma} S$ with the effective surface charge density $\bar{\sigma} = \alpha \sigma$ (α is a scale factor) and the surface area per volume of the NPSM $S = 0.18 \text{ nm}^{-1}$. The intrinsic surface charge density σ is calculated by a temperature-dependent charge regulation model detailed in the Appendix. The largest bulk electrolyte concentration used in our study is 10 mM, so the steric effect is negligible and the ions can be assumed as point charges. Using the assumption of the Boltzmann distribution, ψ^* can be calculated through $\psi^* = -\ln C_i^*/z_i$. As mentioned before, an overlapping EDL can significantly promote electrokinetic effects [15,16]. Therefore, the ratio $\kappa \bar{d}$ of the mean pore size \bar{d} with the Debye length κ^{-1} is applied to judge the level

of EDL overlap, where $\kappa = \sqrt{F^2 z_i^2 C_0^r / \epsilon RT}$ with the permittivity ϵ of the pore solution [34]. When $\kappa \bar{d} \ll 1$, the EDL fully overlaps, while it is negligibly thin when $\kappa \bar{d} \gg 1$. To address the major effects, identical $D_{i,0}(T) \equiv \bar{D}_{i,0}$ and $S_T(T) \equiv \bar{S}_T$ are assumed here, where $\bar{D}_{i,0} = 1.28 D_{i,0}$ and $\bar{S}_T = 0.0008 \text{ K}^{-1}$ at the average temperature $\bar{T} = 308 \text{ K}$; notably, $D_{i,0}$ and S_T slightly vary with T . By inserting Eq. (2) in Eq. (1), the fluxes of ions in an NPSM with a thickness of L and a diameter d_R (detailed in the Appendix) are obtained by:

$$J_i = -\frac{\bar{D}_{i,0}}{GL} \left\{ \Delta C_i + \bar{C}_i \ln [C_i^*(T_{\text{out}})/C_i^*(T_{\text{in}})] + \bar{S}_T \bar{C}_i (T_{\text{out}} - T_{\text{in}}) \right\} \quad (3)$$

where

$$\Delta C_i = C_i^*(T_{\text{out}})C_{i,\text{out}}^r - C_i^*(T_{\text{in}})C_{i,\text{in}}^r \quad (4)$$

$$\bar{C}_i = [C_i^*(T_{\text{out}})C_{i,\text{out}}^r + C_i^*(T_{\text{in}})C_{i,\text{in}}^r] / 2 \quad (5)$$

Furthermore, the concentrations of tracers in the reservoirs at the inlet and outlet are obtained by integrating J_i over time during periods t_s , $C_{i,\text{in}}^r = C_{i,b}^r - \pi d_R^2 / (4V_{\text{in}}) \cdot \int_0^{t_s} J_i dt$ and $C_{i,\text{out}}^r = C_{i,b}^r + \pi d_R^2 / (4V_{\text{out}}) \cdot \int_0^{t_s} J_i dt$.

In the isothermal case, $L = 3.2$ mm, $d_R = 30$ nm, $\bar{d} = 11.1$ nm, $V_{in} = 500$ mL and $V_{out} = 80$ mL. $\bar{D}_{1,0} = D_{1,0} = 2.05 \cdot 10^{-9}$ m²/s and $\bar{D}_{K,0} = D_{K,0} = 1.96 \cdot 10^{-9}$ m²/s at room temperature. The charge regulation model gives $\sigma = -0.0032$ C/m² at $C_0^r = 1$ mM, pH = 6 and $T = 298$ K. There are two unknown parameters G and α in the CTE model. By fitting the isothermal concentration profiles of tracers over time, we can determine the parameters $G = 3.0$ and $\alpha = 0.31$, which is in the classical range of these parameters [35–37]. Fig. 2-A compares the measured and modeled concentrations of potassium and iodide ions in the outlet reservoirs under isothermal conditions, where the lines are calculated based on the CTE model after fitting. These comparisons indicate that the CTE model successfully captures the effect of the EDL on ionic transport in the NPSM, which promotes cation transport while weakening anion transport.

Fig. 2-C shows the effective surface charge density $\bar{\sigma}$ of the NPSM as a function of temperature and pH, which is calculated by the charge regulation model described in the Appendix. Here, $\bar{\sigma}$ tends to be more negative with increasing temperature at the same pH. This means that the surface has a more negative charge, therefore adsorbing more cations at higher temperatures, which is also proved by previous experimental studies [10,18]. Therefore, after applying a thermal gradient to the NPSM, its surface will be inhomogeneously charged. To reduce the fluctuations from experimental data on the results, the mean change rate $\delta C_i = \int_0^{t_s} S_j dt / t_s$ in the reservoir within a time interval $t_s = 1$ day is used here. We analyzed the δC_K of potassium under different nonisothermal conditions by using both the CTE model and experimental data (see Fig. 2-D). We used the average diffusivities at $T = 308$ K in the CTE model: $\bar{D}_{1,0} = 1.28 \times 2.05 \cdot 10^{-9}$ m²/s and $\bar{D}_{K,0} = 1.28 \times 1.96 \cdot 10^{-9}$ m²/s. The results show good agreement between the modeling results and experimental data; as expected, a larger temperature difference ΔT induces a larger δC_K . By increasing the concentration of the background electrolyte NaCl from 1 mM to 10 mM, the EDL becomes thinner and δC_K obviously decreases, revealing the critical role of the EDL on the transport of potassium ions during nanoscale confinement.

Considering Eq. (1), potassium transport is driven by three terms: pure diffusion $J_D^K = -D_{K,e} \nabla C_K$, electrophoresis $J_E^K = -D_{K,e} C_K \nabla \psi^*$ and thermophoresis $J_T^K = -D_{K,e} S_T C_K \nabla T$. Based on the CTE model, we analyzed the flux proportions from these three terms with different thermal gradients (Fig. 3-B). The results indicate that the absolute values of flux from all three terms increase when applying a larger temperature gradient. The absolute value of J_E^K is slightly larger than that of J_D^K , while both of them are much larger than that of J_T^K . Moreover, J_E^K and J_D^K show larger changes than J_T^K when the temperature gradient is changed, while the directions of J_E^K and J_D^K show completely opposite tendencies. As presented in Fig. 2-C, this is caused by the surface charge density gradient on the silica surface, which is induced by the applied temperature gradient. Here, the surface charge density, as well as the related mean electrical potential within the nanopores, reach more negative values on the high-temperature side. Hence, the electric field $-\nabla \psi$ has a direction opposite to the high-temperature side and causes the electrophoresis of cations in the same direction as the electric field. As illustrated by Fig. 3-A, since the higher temperature side can adsorb more cations, the direction of J_D^K is opposite to J_E^K toward the low-temperature side. To quantitatively compare the magnitudes of J_D^K , J_E^K and J_T^K , we analyzed two ratios $|J_E^K/J_D^K|$ and $|(J_E^K + J_D^K)/J_T^K|$ as a function of the dimensionless pore size $\kappa \bar{d}$ in

Fig. 3-C, where C_0^r is changed to achieve the variation of $\kappa \bar{d}$ at a constant $\Delta T = 40$ K. The results show that both $|J_E^K/J_D^K|$ and $|(J_E^K + J_D^K)/J_T^K|$ decrease with increasing $\kappa \bar{d}$. In addition, regarding $\kappa \bar{d}$ up to 10^3 , $|J_E^K/J_D^K|$ is always larger than one (or $|J_E^K| > |J_D^K|$). This means that the sum of $J_E^K + J_D^K$ will be in the same direction as J_E^K despite the opposite directions of J_E^K and J_D^K . $|(J_E^K + J_D^K)/J_T^K|$ will approach zero as $\kappa \bar{d} \rightarrow \infty$, where the EDL thickness is negligibly small compared to the pore diameter. In this case, thermodiffusion is dominant for the net flux, and the EDL effect can be ignored. In contrast, $|(J_E^K + J_D^K)/J_T^K| \rightarrow \infty$ as $\kappa \bar{d} \rightarrow 0$ represents a fully overlapping EDL. This means that an overlapping EDL remarkably magnifies electrophoresis. Hence, $|J_E^K + J_D^K|$ governs the net flux, while thermodiffusion is negligible. For instance, if $\kappa \bar{d} < 10^{-2}$, one finds that $|J_E^K + J_D^K|$ will be larger by one order of magnitude compared to $|J_T^K|$. In our experiments, $\kappa \bar{d} \approx 1.2$ and $|(J_E^K + J_D^K)/J_T^K|$ are approximately 4 for the case of a 1 mM NaCl solution. Regarding the case of a 10 mM NaCl solution, $\kappa \bar{d} \approx 3.9$ while $|(J_E^K + J_D^K)/J_T^K|$ is approximately 1.3, which is slightly larger than 1. Therefore, in both cases, the thermodiffusion contribution to the potassium flux is smaller than from the electrophoresis contribution, which is consistent with our experimental results with a positive δC_K .

3.4. Fully numerical simulations of transport

The electrokinetic response concerned in this work may be different to those with a constant or temperature-dependent value of $D_{i,0}$. In particular, the overlapping EDLs in nanopores could magnify this difference further [38]. It is worth of mentioning that the validity of the Gouy – Chapman model or the Donnan model is questionable as the EDL overlaps in pores [33,39,40]. Such problems can be solved by using fully coupled Poisson-Nernst-Planck (PNP) simulations with the temperature-dependent properties [41]. By applying a temperature gradient through the membrane, the concentrations of tracers will be different in the inlet and outlet reservoirs. After reaching steady state, the concentration difference $\Delta C_s^r = C_{i,out}^r - C_{i,in}^r$ between the two reservoirs will be constant. Using the developed CTE model, the relative concentration difference $\Delta C_s^* = \Delta C_s^r / C_{i,in}^r$ at steady state as a function of temperature difference ΔT can be derived as $J_i = 0$, which gives:

$$\Delta C_s^* = \frac{2C_K^*(T_{in}) + C_K^*(T_{in}) \ln[C_K^*(T_{in})/C_K^*(T_{out})]}{2C_K^*(T_{out}) - C_K^*(T_{out}) \ln[C_K^*(T_{in})/C_K^*(T_{out})]} - 1 \quad (6)$$

Fig. 4-A shows that ΔC_s^* increases with an increasing ΔT . Herein, the results (solid line) by our model depend on the average diffusivities and the mean concentrations of ions in Eq. (6) at pH = 8 and $C_0^r = 0.01$ M. We also simulated the same processes by numerically solving the fully coupled PNP equations. The main process of our numerical framework is described in the Appendix. The simulation results (circle symbols in Fig. 4-A) agree well with the solution from the CTE model, as $|\Delta T| < 35$ K, which again supports the accuracy of the CTE model. Fig. 4-B presents the simulated electrical potential distribution in a three-dimensional nanoporous membrane under applying a temperature field, where the pores with a higher temperature show a lower electrical potential.

Our experimental and modeling results reveal the critical impact of an overlapping EDL on thermodiffusion in nanoscale por-

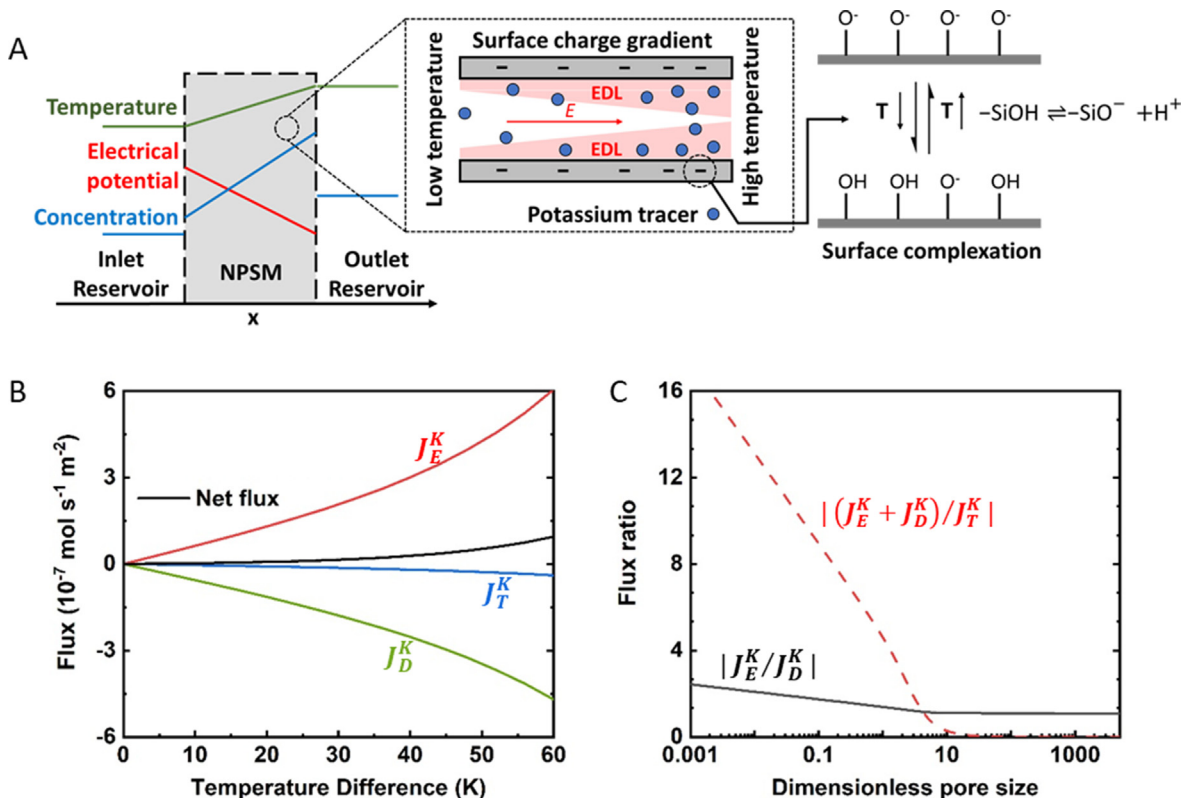


Fig. 3. Mechanism and flux proportions after applying temperature gradients. (A) The figure on the right side shows the mean concentration, electrical potential and temperature profiles within the NPSM and a microscopic sketch of the potassium tracer and EDL in a single nanopore with an applied temperature gradient (middle); the red areas represent the EDL. The side with a high temperature has a larger EDL thickness, so it can adsorb more potassium ions. The red arrow denotes the inner electrical field E . The figure on the left side shows the patterns of surface complexations with respect to temperature. (B) Potassium flux due to pure diffusion $J_D^K = -D_{K,e} \nabla C_K$, electroosmosis $J_E^K = -D_{K,e} C_K \nabla \psi'$, and thermophoresis $J_T^K = -D_{K,e} S_T C_K \nabla T$, and the net flux as a function of ΔT (the positive direction of flux is along the positive x-axis in (A)). (C) Flux ratios $|J_E^K/J_D^K|$ and $|(J_E^K + J_D^K)/J_T^K|$ as a function of the dimensionless pore size κd (at $\Delta T = 40$ K). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

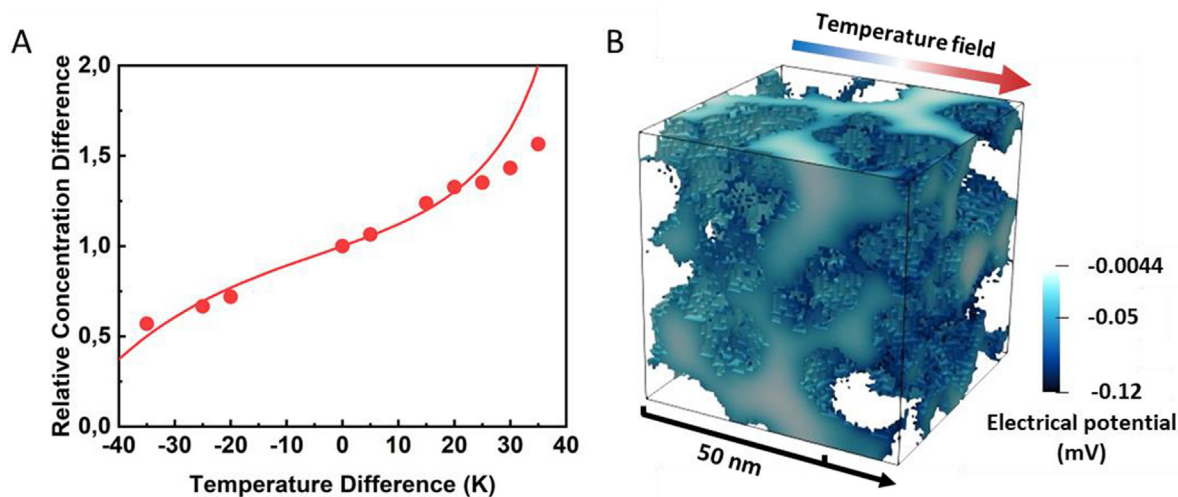


Fig. 4. Modeling results of the nonisothermal diffusional at steady state. (A) Relative concentration difference $\Delta C_s^c = \Delta C_s^c / C_{in}^c$ as a function of the temperature difference ΔT at steady state, calculated by our CTE model (solid line) and numerical framework (circle symbols). (B) Simulated three-dimensional distribution of the electrical potential under a temperature gradient ($\Delta T = 35$ K). Solid phase is invisible.

ous media. With a temperature gradient, the induced surface charge gradient at the solid–liquid interface will create an inhomogeneous EDL structure along the transport direction, which could significantly enhance ionic transport. Furthermore, our findings have the potential to become a fundamental method for manipulating macroscopic ion transport. Inspired by the thermal metamaterials

developed several years ago [42–45], the mechanisms in this study could be implemented for diffusional metamaterials, where ionic diffusion is governed by a temperature field. For instance, if a spot-like heater (the temperature field shown in Fig. 5-B) is applied to a 2D ideal nanoscale structure (Fig. 5-A), the cationic tracers could also accumulate in this region; thus, a

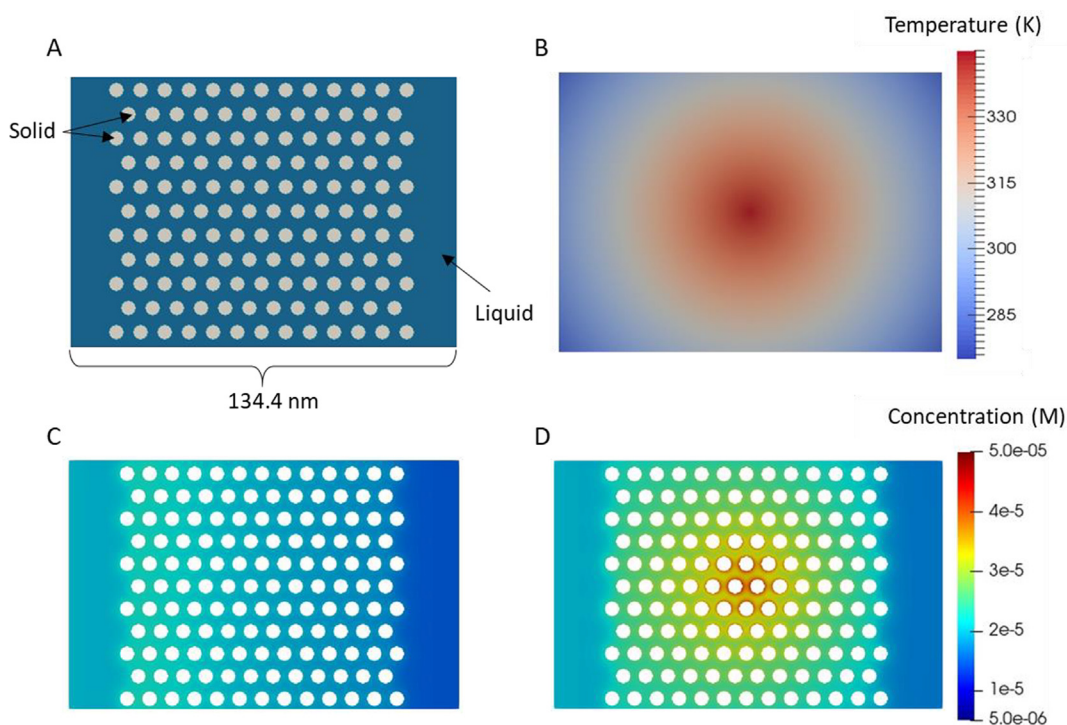


Fig. 5. Manipulate ionic transport in nanoporous media by controlling the temperature field. (A) 2D nanoporous structure in our simulation. (B) Steady-state temperature field if the heater is on. (C) and (D) Simulated distribution of the cationic tracer concentration when turning the heater on and off (also see Movie S1 for comparison).

spot-like heater acts similar to a thermal concentrator. Fig. 5-C and Fig. 5-D compare the PNP simulations for concentrating the cationic tracers by turning the heater on or off (also see more details in Movie S1 for comparison). The simulations show that the cationic tracer is obviously concentrated in the center of this nanoporous medium when it is heated, which can potentially be used to separate contaminants.

4. Conclusion

Thermodiffusion in nanoporous media is an important fundamental process in many natural and technical settings. We demonstrate that the gradient of the surface charge density induced by the applied temperature field leads to electrophoretic ionic mobility, which may promote up to one order of magnitude larger ionic mobility than classical thermophoretic mobility. Both experimental and modeling results in this study indicate the remarkable effect of temperature on the transport of nanoconfined ions. Furthermore, our results provide a critical and robust mechanism to manipulate ionic transport, which can be applied in energy conversion, species separation/collection, or desalination. This manipulation method does not need a subtly designed structure, only requiring the application of a suitable temperature field on nanoporous materials. In addition, the surfaces of most mineral materials (such as clay, silica or calcite) are naturally charged when in contact with an electrolyte, and the surface charge automatically changes with varying temperature, which is easier than other manipulation methods [16,46,47]. Therefore, compared with other manipulation methods, this mechanism is convenient, nondestructive and extensive.

CRediT authorship contribution statement

Yuankai Yang: Methodology, Investigation, Writing – original draft. **Xudong Zhang:** Investigation, Writing – original draft. **Zhi-**

guo Tian: Investigation. **Guido Deissmann:** Writing – review & editing. **Dirk Bosbach:** Writing – review & editing. **Peng Liang:** Supervision, Writing – review & editing. **Moran Wang:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2022.03.077>.

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