Supplementary Information

A New Paradigm for Brine Thermodynamics: Inverse Electrochemical Probing of Activity Using Reverse Electrodialysis

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Supplementary Information

Supplementary Note S1. Seasonal thermodynamic and transport property calculations

This work is entirely model-based. Seasonal solution properties were generated by coupling multi-ion Pitzer thermodynamics with a permselectivity-corrected reverse electrodialysis (RED) electrochemical model. For each season, the thermodynamic state of both the hypersaline (concentrated) stream and treated wastewater (TWW; dilute) stream was characterized in terms of mean ionic activity and associated transport properties (electrical conductivity). The resulting seasonal activity–conductivity pairs are tabulated in Tables S3 and S4.

S1.1 Seasonal forcing and inputs

For each season $s \in \{\text{Summer, Autumn, Winter, Spring}\}$, the following inputs were prescribed: (i) temperature T_s (K), converted from Celsius via

$$T_s = T_{C,s} + 273.15; \tag{1}$$

(ii) ionic compositions expressed as molalities $m_{i,s}$ ($\mathrm{mol\,kg^{-1}}$) for the hypersaline and TWW streams; (iii) multi-ion Pitzer interaction parameters from the literature; and (iv) RED system parameters including stack size N, average permselectivity α, and constants R and F.

S1.2 Ionic strength calculation

For each stream and season, the ionic strength was computed as

$$I_s = \frac{1}{2}\sum_i m_{i,s} z_i^2, \tag{2}$$

where $m_{i,s}$ and z_i are the molality and charge of ion i, respectively.

S1.3 Mean ionic activity coefficients

Mean ionic activity coefficients $\gamma_{\pm,s}$ were computed using the multi-ion Pitzer formalism, in which

$$\ln \gamma_{\pm,s} = f(I_s, T_s) + \sum (\text{interaction terms}), \tag{3}$$

combining long-range electrostatic and short-range ion–ion interactions.

S1.4 Mean ionic activity calculation

Mean ionic activities were computed on the molality scale as

$$a_{\pm,s} = \gamma_{\pm,s} \left(\frac{m_s}{m^\circ} \right), \qquad m^\circ = 1 \text{ mol kg}^{-1}. \tag{4}$$

For the hypersaline stream this yields an effective activity $a_{\mathrm{H}}^{(\mathrm{eff})}$, while the dilute stream activity is denoted a_{TWW}.

S1.5 Electrical conductivity computation

Electrical conductivity κ_s was computed consistently with the same thermodynamic state defined by $(T_s, m_{i,s})$. Conductivity was used to parameterize the channel resistance via

$$R_{\mathrm{ch},s} = \frac{l}{\kappa_s A}, \tag{5}$$

where l is channel length and A the channel cross-sectional area.

S1.6 Link to inverse thermodynamic probe framework

The seasonal activities reported in Tables S3 and S4 enter the permselectivity-corrected RED voltage expression

$$E_{\mathrm{OCV},s} = \alpha N \frac{R T_s}{z F} \ln \left(\frac{a_{\pm,c,s}}{a_{\pm,d,s}} \right). \tag{6}$$

Deviations between ideal and non-ideal voltage predictions encode non-ideal thermodynamic information and enable inference of activity-coefficient effects from electrical observables.

S2. Multi-ion thermodynamic model for Aral Sea brine

The ionic composition of the Aral Sea brine used in this work is summarised in Table S1. Concentrations are expressed as molality m_i (mol kg^{-1} of water).

The ionic strength of the brine is

$$I = \frac{1}{2} \sum_i m_i z_i^2 = 5.13 \text{ mol kg}^{-1}. \tag{7}$$

At this ionic strength, ion non-ideality is described using the multi-ion Pitzer formulation. For ion i, the activity coefficient is

$$\ln \gamma_i = z_i^2 f(I) + \sum_j m_j B_{ij}(I) + \sum_{j,k} m_j m_k C_{ijk}, \tag{8}$$

Table 1: Ionic composition and transport parameters for Aral Sea brine at 25 °C.

Ion	c ($\mathrm{g\,L^{-1}}$)	M ($\mathrm{g\,mol^{-1}}$)	C ($\mathrm{mol\,L^{-1}}$)	z	m ($\mathrm{mol\,kg^{-1}}$)	$0.5\,mz^2$	λ_i^0 ($\mathrm{S\,m^2\,mol^{-1}}$)
$\mathrm{Cl^-}$	84.62	35.45	2.387	-1	2.3978	1.1989	0.007635
$\mathrm{SO_4^{2-}}$	69.95	96.06	0.728	-2	0.7315	1.4630	0.016000
$\mathrm{HCO_3^-}$	0.88	61.02	0.0144	-1	0.0145	0.0072	0.004450
$\mathrm{Na^+}$	62.43	22.99	2.716	$+1$	2.7278	1.3639	0.005010
$\mathrm{K^+}$	3.82	39.10	0.0977	$+1$	0.0981	0.0491	0.007350
$\mathrm{Ca^{2+}}$	0.35	40.08	0.0087	$+2$	0.0088	0.0175	0.011900
$\mathrm{Mg^{2+}}$	12.44	24.31	0.512	$+2$	0.5140	1.0281	0.010600

where $f(I)$ is the Debye–Hückel long-range term, B_{ij} are binary interaction terms, and C_{ijk} are ternary interaction terms.

For RED calculations, we define an effective charge-equivalent activity of the high-salinity stream as

$$a_{\mathrm{H}}^{(\mathrm{eff})} \equiv \sum_i |z_i|\, a_i = \sum_i |z_i|\, m_i \gamma_i. \tag{9}$$

Evaluated at 25 °C, this yields

$$a_{\mathrm{H}}^{(\mathrm{eff})}(25^\circ\mathrm{C}) \approx 1.1\ \mathrm{mol\,kg^{-1}}. \tag{10}$$

S3. Conductivity of Aral brine and treated wastewater

The equivalent fraction of ion i is

$$y_i = \frac{|z_i| m_i}{\sum_j |z_j| m_j}, \qquad \sum_j |z_j| m_j = 7.75\ \mathrm{mol\,kg^{-1}}. \tag{11}$$

The mixture limiting equivalent conductance is

$$\bar{\lambda}^0 = \sum_i y_i \lambda_i^0 \approx 8.68 \times 10^{-3}\ \mathrm{S\,m^2\,mol^{-1}}. \tag{12}$$

For the purpose of estimating electrical conductivity, a charge-equivalent volumetric concentration is introduced as

$$c_{\mathrm{eq}}^0 = \left(\sum_i |z_i| m_i\right) \times 10^3 = 7.75 \times 10^3\ \mathrm{mol\,m^{-3}}, \tag{13}$$

yielding a limiting conductivity

$$\kappa^0 = \bar{\lambda}^0 c_{\mathrm{eq}}^0 \approx 67\ \mathrm{S\,m^{-1}}. \tag{14}$$

To account for ion pairing and mobility reduction at high ionic strength, an empirical reduction factor is calibrated against measured conductivity:

$$f_\kappa = \frac{\kappa_{\mathrm{meas}}}{\kappa^0} = \frac{22.4}{67} \approx 0.33, \tag{15}$$

leading to the effective conductivity used in the RED model,

$$\kappa_{\mathrm{sea}}(25^\circ\mathrm{C}) = f_\kappa \kappa^0 \approx 22.4\ \mathrm{S\,m^{-1}}. \tag{16}$$

For treated wastewater (TWW), a NaCl-equivalent concentration of $C_{\mathrm{TWW}} = 26\ \mathrm{mol\,m^{-3}}$ is assumed. The Davies equation gives $\gamma_\pm \approx 0.86$, yielding

$$a_{\mathrm{TWW}}(25^\circ\mathrm{C}) = m\gamma_\pm \approx 0.0223\ \mathrm{mol\,kg^{-1}}. \tag{17}$$

Based on field data, the baseline conductivity is taken as

$$\kappa_{\mathrm{TWW}}(25^\circ\mathrm{C}) = 0.263\ \mathrm{S\,m^{-1}}. \tag{18}$$

S4. Seasonal temperature dependence

Seasonal-average temperatures were used to recompute activities and conductivities following the same workflow. Activities were updated as

$$a(T) = a(T_{\mathrm{ref}})\frac{T}{T_{\mathrm{ref}}}, \qquad T_{\mathrm{ref}} = 298.15\ \mathrm{K}, \tag{19}$$

and conductivities using a linear temperature coefficient

$$\kappa(T) = \kappa(T_{\mathrm{ref}})\left[1 + \alpha_\kappa (T_C - 25)\right], \qquad \alpha_\kappa = 0.02\ ^\circ\mathrm{C}^{-1}. \tag{20}$$

Table 2: Seasonal-average activities and conductivities used in the RED model.

Season	T_C (°C)	T (K)	$a_{\mathrm{H}}^{(\mathrm{eff})}$	a_{TWW}	κ_{sea} ($\mathrm{S\,m^{-1}}$)	κ_{TWW} ($\mathrm{S\,m^{-1}}$)
Summer	26.41	299.56	1.105	0.0224	23.03	0.270
Autumn	12.58	285.73	1.054	0.0214	16.84	0.198
Winter	-0.84	272.31	1.005	0.0204	10.82	0.127
Spring	14.01	287.16	1.059	0.0215	17.48	0.205

Table 3: Electrical conductivity as a function of mean ionic activity (Hypersaline seawater).

Season	Mean ionic activity, $a_{\mathrm{H}}^{(\mathrm{eff})}$ ($\mathrm{mol\,kg^{-1}}$)	Electrical conductivity, κ_{sea} ($\mathrm{S\,m^{-1}}$)
Summer	1.105	23.03
Autumn	1.054	16.84
Winter	1.005	10.82
Spring	1.059	17.48

Table 4: Electrical conductivity as a function of mean ionic activity (Treated wastewater).

Season	Mean ionic activity, a_{TWW} ($\mathrm{mol\,kg^{-1}}$)	Electrical conductivity, κ_{TWW} ($\mathrm{S\,m^{-1}}$)
Summer	0.0224	0.270
Autumn	0.0214	0.198
Winter	0.0204	0.127
Spring	0.0215	0.205

Abbreviations

Table 1: List of abbreviations used in this study.

Abbreviation	Definition
RED	Reverse Electrodialysis
OCV	Open-circuit voltage
E_{OCV}	Open-circuit voltage of a RED stack
$E_{\mathrm{OCV}}^{\mathrm{ideal}}$	Ideal Nernstian open-circuit voltage
$E_{\mathrm{OCV}}^{\text{ideal-sol}}$	Ideal-solution open-circuit voltage
ΔE_γ	Voltage deviation due to activity-coefficient effects
R	Universal gas constant
T	Absolute temperature
T_C	Temperature in degrees Celsius
F	Faraday constant
z	Effective ionic charge number
N	Number of membrane cell pairs in the RED stack
α	Average membrane permselectivity
a_i	Ionic activity of species i
$a_\pm$	Mean ionic activity
γ_i	Activity coefficient of ion i
$\gamma_\pm$	Mean ionic activity coefficient
m_i	Molality of ion i
m°	Standard molality (1 mol kg^{-1})
$a_{\mathrm{H}}^{(\mathrm{eff})}$	Effective charge-equivalent activity of the hypersaline stream
TWW	Treated wastewater
I	Ionic strength
Pitzer model	Thermodynamic model for non-ideal electrolyte solutions
B_{ij}	Binary Pitzer interaction parameter
C_{ijk}	Ternary Pitzer interaction parameter
κ	Electrical conductivity
κ_{sea}	Electrical conductivity of hypersaline seawater
κ_{TWW}	Electrical conductivity of treated wastewater
λ_i^0	Limiting equivalent conductance of ion i
$\bar{\lambda}^0$	Mixture limiting equivalent conductance
y_i	Charge-equivalent fraction of ion i
c_{eq}^0	Charge-equivalent volumetric concentration
f_κ	Empirical mobility-reduction factor
R_{ch}	Channel (solution) resistance
A	Channel cross-sectional area
l	Channel length
W_{rev}	Reversible electrochemical work
ΔG_{mix}	Gibbs free energy of mixing