Electronic Supplementary Material (ESI) for Lab on a Chip.

Electronic Supplementary Information

Modeling Electrical Double-Layer Effects for Microfluidic Impedance Spectroscopy from 100 kHz to 110 GHz

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Figures and Tables:

Uncertainty Calculations:

Multiline TRL calibration [1] gives uncertainty estimates for the propagation constants γ_{tot} and γ_o for each frequency value, and the series resistor calibration [2] gives uncertainties in the capacitance per-unit-length for the air-loaded lines C_o for all frequency values. We propagate these uncertainties through Eq. 1, yielding uncertainty estimates for the device admittance terms G_{tot} and C_{tot} at each frequency value. Due to limitations in the multiline TRL approach, at lower frequencies, we only used this approach to estimating measurement uncertainties above 5 GHz. Below 5 GHz, we used the standard deviation of measurements of all four channel-loaded transmission lines to estimate the uncertainty in G_{tot} and C_{tot} .

All Calibrated Saline Data:

In Fig. S1 we display all measured admittance data. Data is presented in terms of the total capacitance (C_{tot}) and conductance (G_{tot}/ω) of the microfluidic lines filled with Air, DI water, and all saline concentrations, at the three measured temperatures (9.5℃, 28.6℃, and 47.6℃).

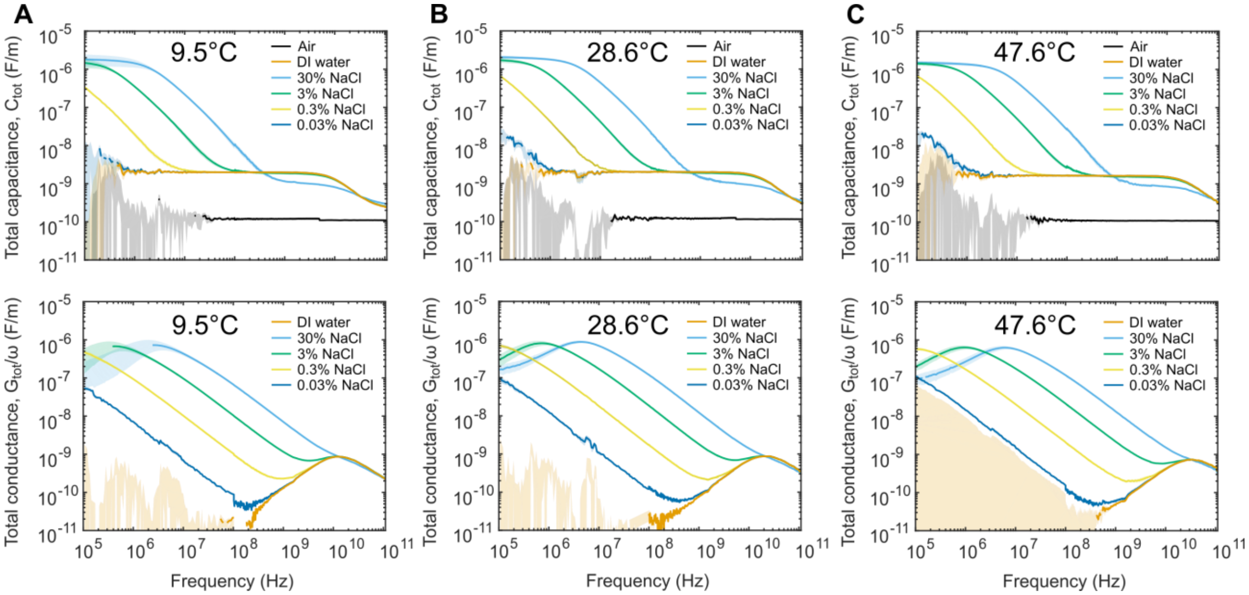

Figure S1. Calibrated admittance per-unit-length data for all samples. (A) Data at 9.5℃. (B) Data at 28.6℃. (C) Data at 47.6℃.

Fit of the Fluid Admittance:

We fit the measured admittance data for all temperatures and saline concentrations to a Cole-Cole function (Eq. 5) that includes a term to describe the ionic conductivity of the fluid. The relevant fitting parameters for the Cole-Cole model were C_w, C_∞, τ_w, $1-\alpha_w$, and G_σ. The resulting values of the fitting parameters are given in Table S1. Additionally, in Fig. S2, we plot the admittance and corresponding permittivity of the fluid with the conductivity of the fluid removed. Figure S2 graphically illustrates the effect of saline concentration and temperature on the permittivity of water. A Cole-Cole description was used to model the water relaxation, instead of a bimodal Debye relaxation (as suggested by Buchner [3]), as the Cole-Cole function produced an acceptable fit with fewer fit parameters for all solutions studied. In Table S2, we also give the ionic conductivity of the saline solutions (σ) for all concentrations and temperatures. As stated in the main text, these values are determined by the following expression: $kG_\sigma = \sigma$.

For reference, the admittance parameters in Table S1 are also given in terms of the fluid permittivity, using the dimensionless geometric factor k introduced in the text. The permittivity of DI water, required to determine k, came from the literature [3]. To determine values for the permittivity of DI water at specific temperatures we fit the aggregated data from Fernandez et al. to the following equation:

$$\epsilon_r = a + bT + cT^2,$$

Equation S1.

similar to that used by Malmberg and Maryott [4], where T is the temperature in Kelvin, and ϵ_r is the relative permittivity of water at zero frequency. The fit resulted in a = 2.46 x 10^2, b = -7.62 x 10^{-1} 1/K, c = 6.76 x 10^{-4} 1/K^2. For the temperatures used in this work, we calculate literature values for the DI water permittivity of 84.6, 76.9, and 70.3 at 9.5 C, 28.6 C and 47.6 C, respectively. These permittivity values are consistent with those that result from the equation proposed by Pátek et al. [5], within uncertainties.

Table S1. Fluid admittance per-unit-length fitting parameters using Eq. 5, as well as the intrinsic parameters describing the Cole-Cole fit to the fluid permittivity. The values for the relative permittivity of DI water are from the literature and are marked with an asterisk (*). These values were used to determine the geometric factor *k*.

Temp (℃)	W_{NaCl} (%)	**C_w (F/m)**	**Relative permittivity water (*f*=0)**	**C_∞ (F/m)**	**Relative permittivity water (*f*=∞)**	**τ_w (s)**	**1-α_w**	**G_σ (S/m)**
9.5 ℃	30	**1.07 x10^{-9}**	**45.8**	**2.09 x10^{-10}**	**5.7**	**9.41 x10-^{12}**	**0.849**	**4.15 x10^{1}**
	3	**1.80 x10^{-9}**	**79.6**	**2.09 x10^{-10}**	**5.7**	**1.18 x10^{-11}**	**0.980**	**6.24**
	0.3	**1.90 x10^{-9}**	**84.3**	**2.13 x10^{-10}**	**5.9**	**1.22 x10^{-11}**	**0.992**	**5.91 x10^{-1}**
	0.03	**1.91 x10^{-9}**	**84.6**	**2.16 x10^{-10}**	**6.0**	**1.22 x10^{-11}**	**0.997**	**4.02 x10^{-2}**
	DI water	**1.91 x10^{-9}**	**84.6***	**2.16 x10^{-10}**	**6.0**	**1.22 x10^{-11}**	**0.998**	**<1x10^{-2}**
28.6 ℃	30	**9.06 x10^{-9}**	**38.0**	**2.00 x10^{-10}**	**5.3**	**4.96 x10-^{12}**	**0.896**	**6.50 x10^{1}**
	3	**1.64 x10^{-9}**	**72.1**	**1.87 x10^{-10}**	**4.7**	**6.93 x10-^{12}**	**0.974**	**9.47**
	0.3	**1.74 x10^{-9}**	**76.6**	**1.92 x10^{-10}**	**4.9**	**7.13 x10-^{12}**	**0.988**	**9.29 x10^{-1}**
	0.03	**1.74 x10^{-9}**	**76.9**	**1.93 x10^{-10}**	**4.9**	**7.14 x10-^{12}**	**0.990**	**6.20 x10^{-2}**
	DI water	**1.74 x10^{-9}**	**76.9***	**1.92 x10^{-10}**	**4.9**	**7.16 x10-^{12}**	**0.990**	**<1x10^{-2}**
47.6 ℃	30	**8.88 x10^{-10}**	**37.2**	**1.90 x10^{-10}**	**4.8**	**3.43 x10-^{12}**	**0.926**	**8.44 x10^{1}**
	3	**1.51 x10^{-9}**	**66.2**	**1.63 x10^{-10}**	**3.6**	**4.56 x10-^{12}**	**0.965**	**1.31 x10^{1}**
	0.3	**1.60 x10^{-9}**	**70.2**	**1.67 x10^{-10}**	**3.7**	**4.65 x10-^{12}**	**0.979**	**1.25**
	0.03	**1.60 x10^{-9}**	**70.3**	**1.85 x10^{-10}**	**4.6**	**4.72 x10-^{12}**	**0.992**	**8.94 x10^{-2}**
	DI water	**1.60 x10^{-9}**	**70.3***	**1.80 x10^{-10}**	**4.6**	**4.69 x10-^{12}**	**0.993**	**<1x10^{-2}**

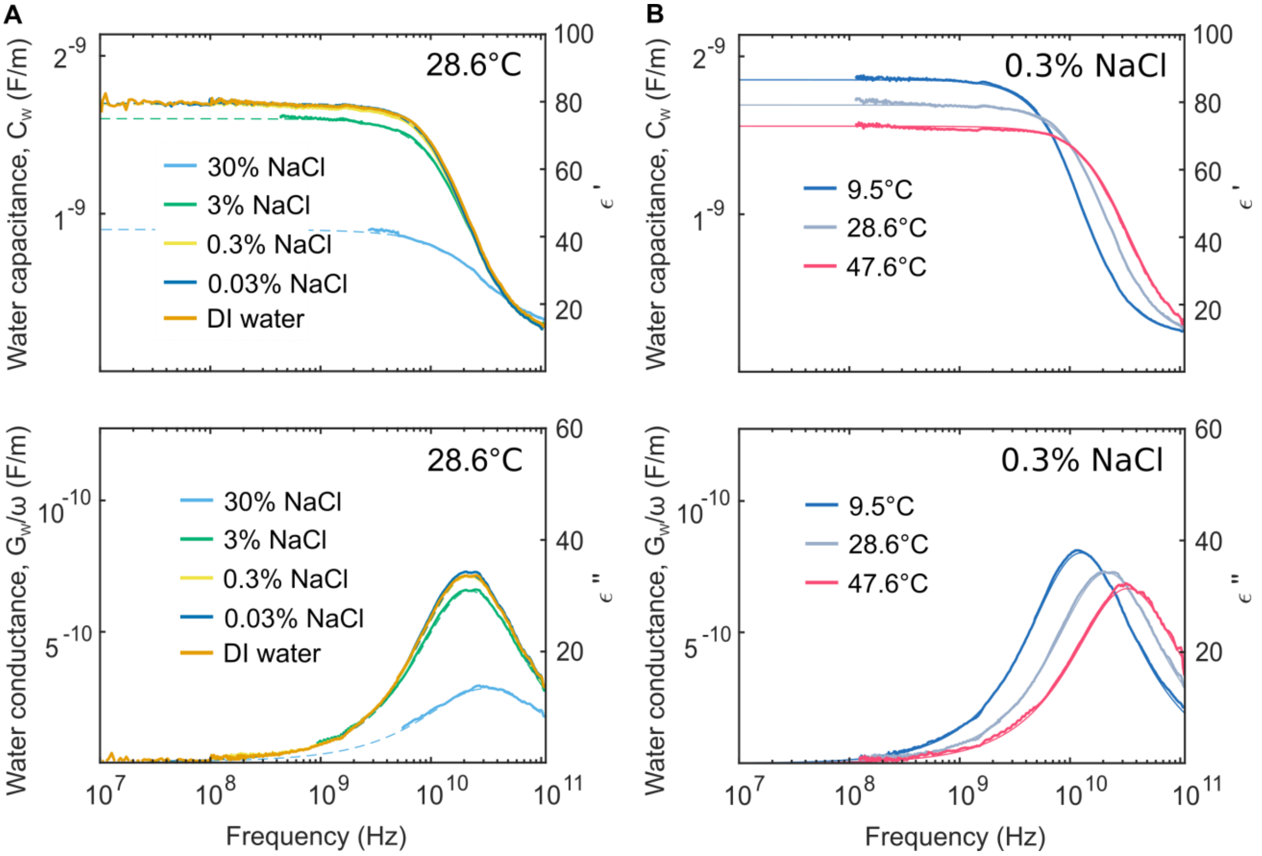

Figure S2. Water admittance per unit length. (A) water admittance per unit length with NaCl concentrations at a temperature of 28.6℃. (B) Change in water admittance per unit length with temperature for a concentration of 0.3% NaCl by weight. Permittivity values on the right hand vertical axes are calculated based on the dimensionless geometrical parameter *k* introduced in the main text.

Table S2. Measured ionic conductivity of saline solutions.

Temp (℃)	W_{NaCl} (%)	σ (S/m)
9.5	30	1.71×10^{1}
	3	2.58
	0.3	2.44×10^{-1}
	0.03	1.66×10^{-2}
	<0.01	$< 1 \times 10^{-2}$
28.6	30	2.681×10^{1}
	3	3.91
	0.3	3.841×10^{-1}
	0.03	2.561×10^{-2}
	<0.01	$< 1 \times 10^{-2}$
47.6	30	3.491×10^{1}
	3	5.40
	0.3	5.181×10^{-1}
	0.03	3.691×10^{-2}
	<0.01	$< 1 \times 10^{-2}$

Fits of the Electrical Double-layer Admittance:

The admittance of the EDL is extracted from the measured device admittance using Eq. 4 in the main text. The resulting EDL admittance is fit using Eqs. 6 and 7. In Fig. S3 we show the fit of the extracted EDL admittance with the extracted EDL data. The EDL relaxation capacitance C_D compared to the CPE capacitance C_{CPE} at 100 kHz (Table S3) demonstrates similar magnitudes from both effects. The CPE capacitance at 100 kHz is approximately half that of the EDL relaxation capacitance C_D.

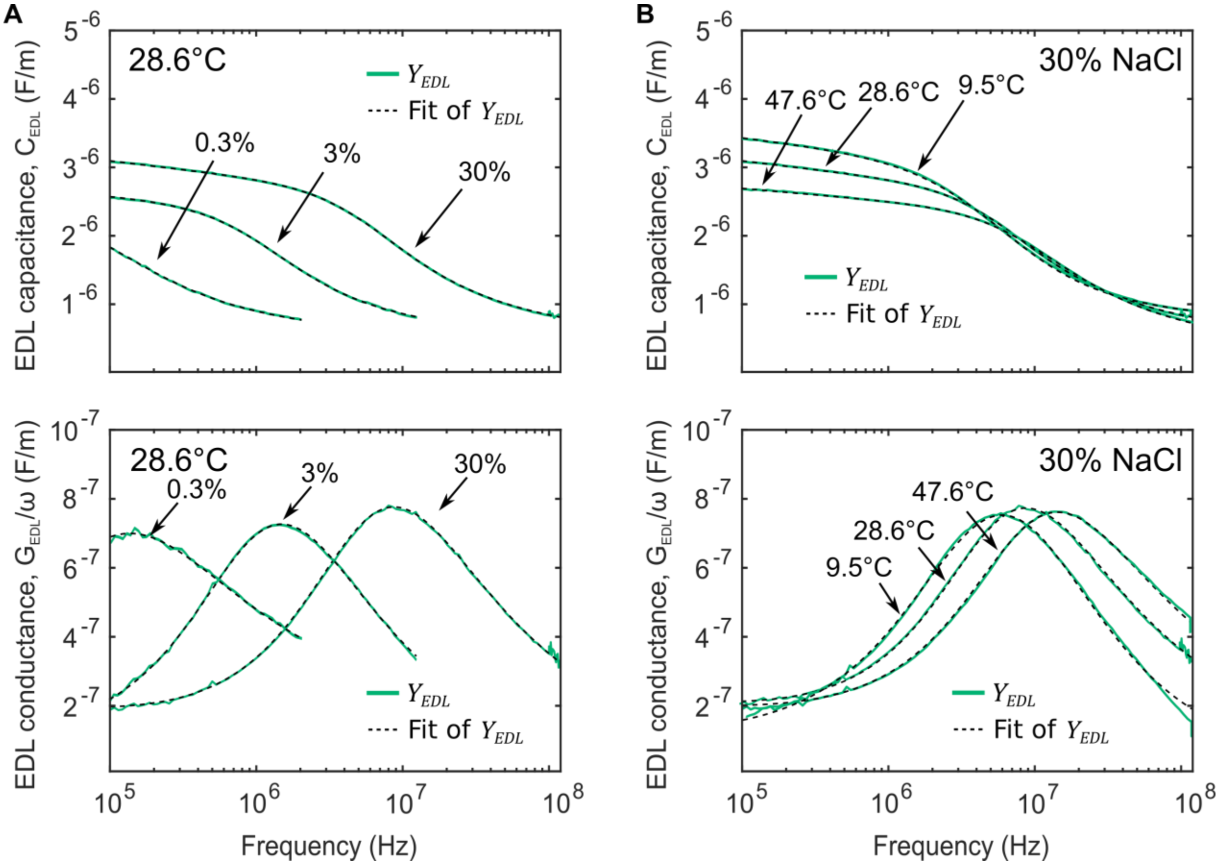

Figure S3. Extracted EDL admittance per unit length and fit. (A) Electrical double layer (EDL) admittance per unit length for different NaCl concentrations at 28.6℃. (B) Electrical double layer (EDL) admittance per unit length for different temperatures for a concentration of 30% NaCl by weight.

Table S3. Capacitance contributions from both the Debye and CPE components of the EDL.

Temp (℃)	W_{NaCl} (%)	**C_D (F/m)**	**C_{CPE} (F/m) @1x10^5 Hz**
9.5 ℃	**30**	**1.91 x10^{-6}**	**1.15 x10^{-6}**
	3	**2.25 x10^{-6}**	**8.00 x10^{-7}**
28.6 ℃	**30**	**1.93 x10^{-6}**	**1.23 x10^{-6}**
	3	**2.02 x10^{-6}**	**8.77 x10^{-7}**
47.6 ℃	**30**	**1.87 x10^{-6}**	**9.95 x10^{-7}**
	3	**1.93 x10^{-6}**	**8.55 x10^{-7}**

References:

[1] D. F. Williams, C. M. Wang, and U. Arz, “An optimal multiline TRL calibration algorithm,” in *IEEE MTT-S International Microwave Symposium Digest, 2003*, 2003, vol. 3, pp. 1819–1822 vol.3.

[2] N. D. Orloff *et al.*, “A Compact Variable-Temperature Broadband Series-Resistor Calibration,” *IEEE Trans. Microw. Theory Tech.*, vol. 59, no. 1, pp. 188–195, Jan. 2011.

[3] D. P. Fernández, Y. Mulev, A. R. H. Goodwin, and J. M. H. L. Sengers, “A Database for the Static Dielectric Constant of Water and Steam,” *J. Phys. Chem. Ref. Data*, vol. 24, no. 1, pp. 33–70, Jan. 1995.

[4] C. G. Malmberg and A. A. Maryott, “Dielectric Constant of Water from 0 to 100 C,” *Journal of Research of the National Bureau of Standards*, vol. 56, no. 1, 1956.

[5] J. Pátek, J. Hrubý, J. Klomfar, M. Součková, and A. H. Harvey, “Reference Correlations for Thermophysical Properties of Liquid Water at 0.1 MPa,” *J. Phys. Chem. Ref. Data*, vol. 38, pp. 21–29, Mar. 2009.