

Supporting Information (Part 3):

Determination of the Exact Particle Radius Distribution for Silica Nanoparticles via Capillary Electrophoresis and Modelling the Electrophoretic Mobility with a Modified Analytic Approximation

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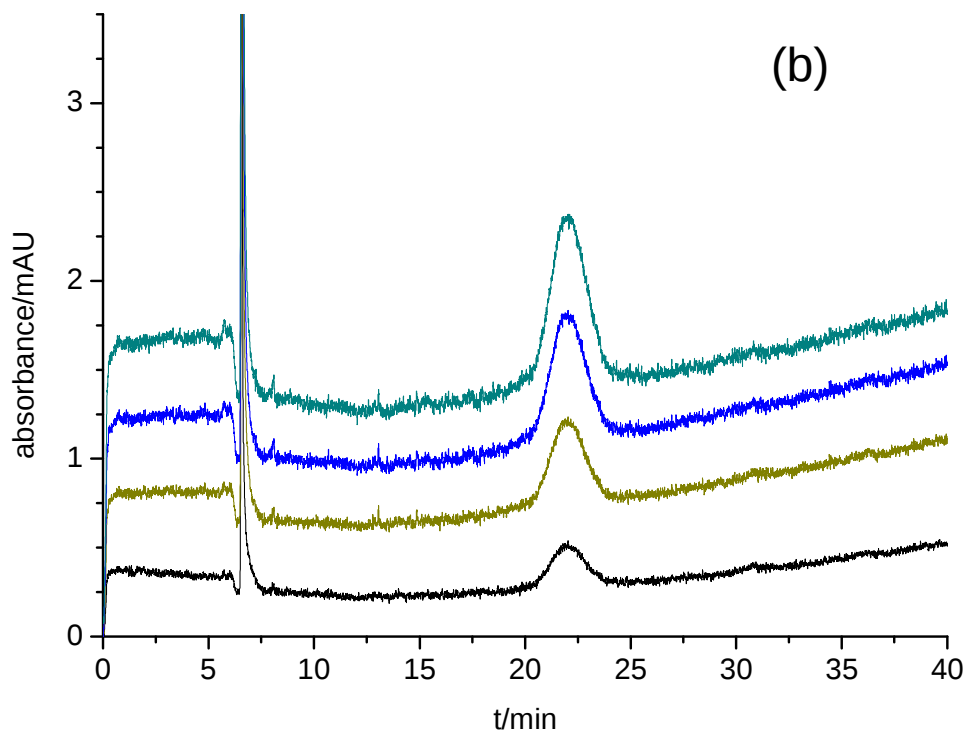
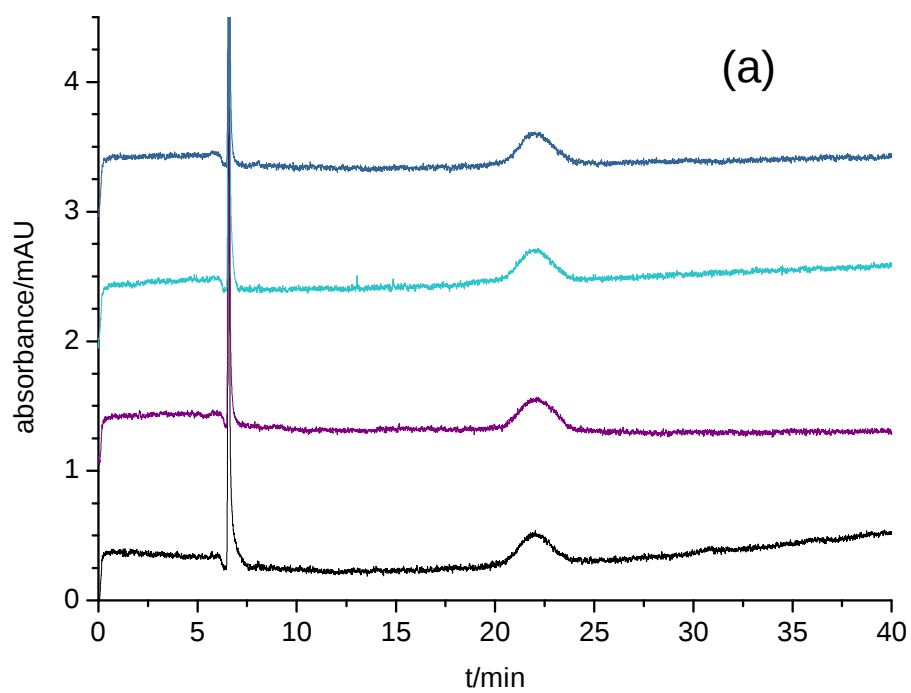
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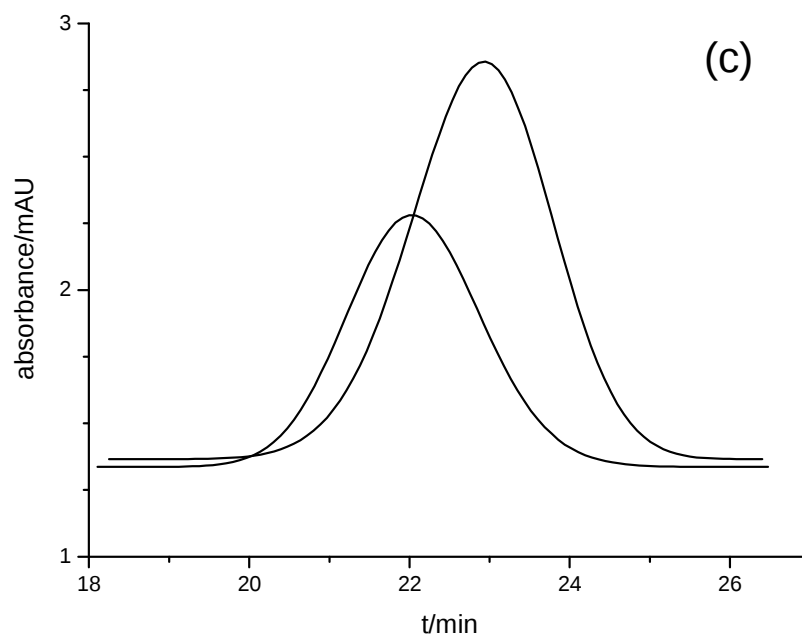
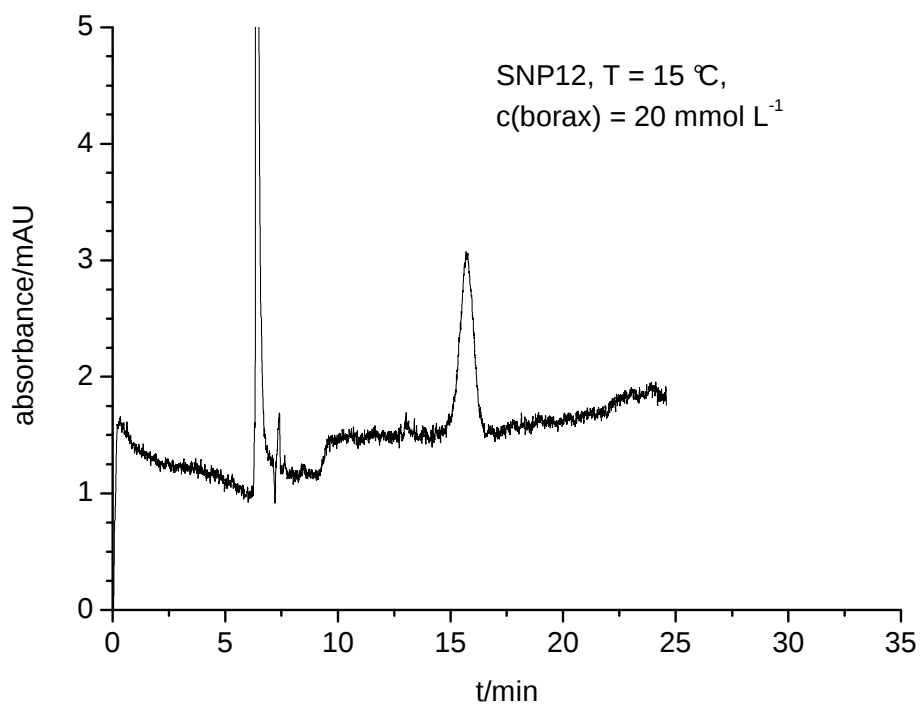
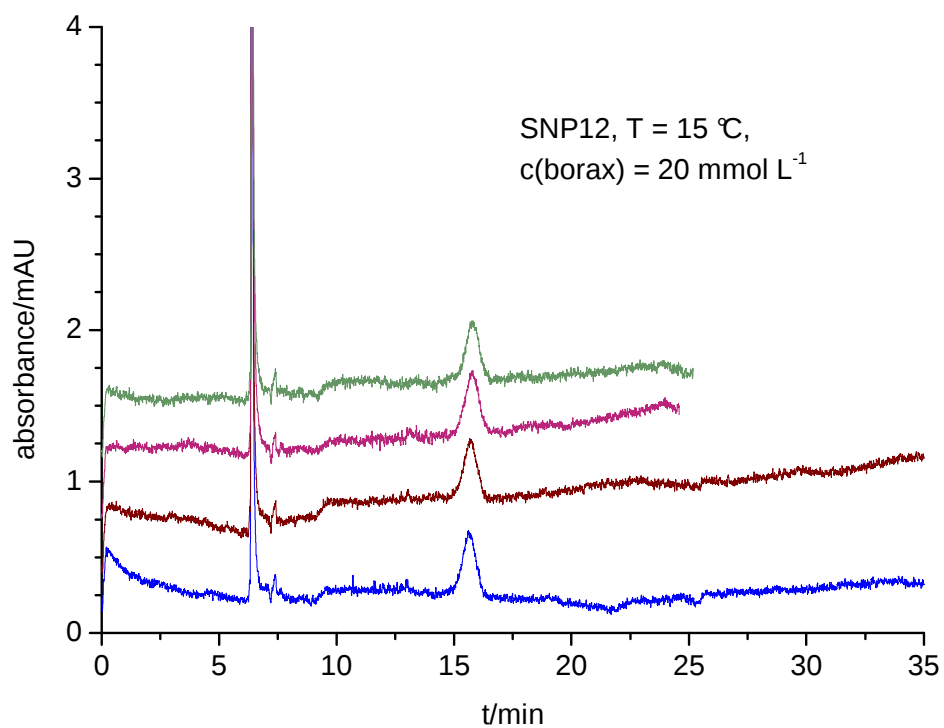
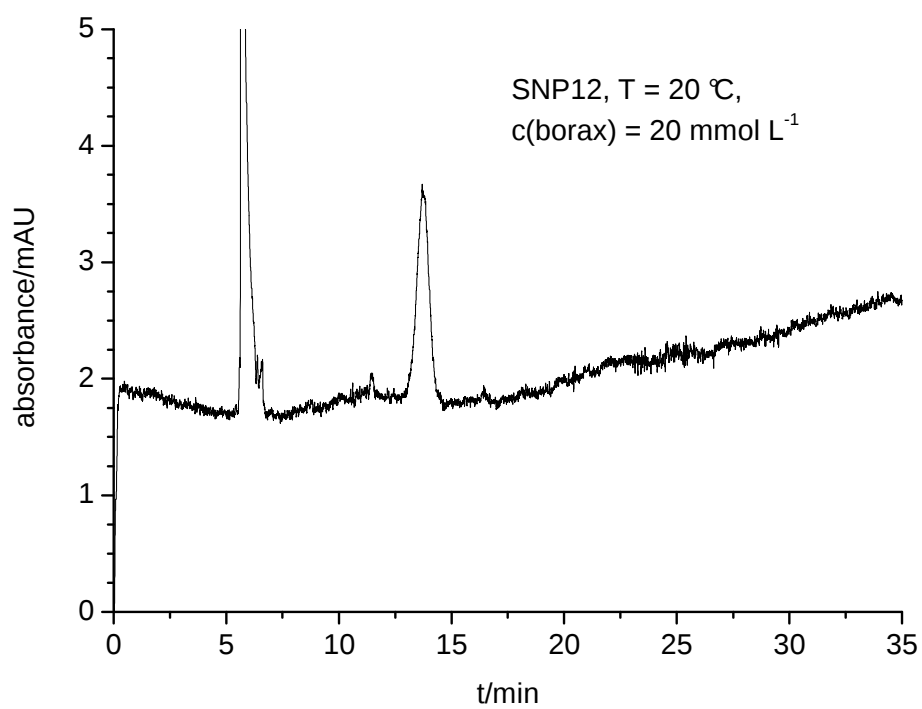
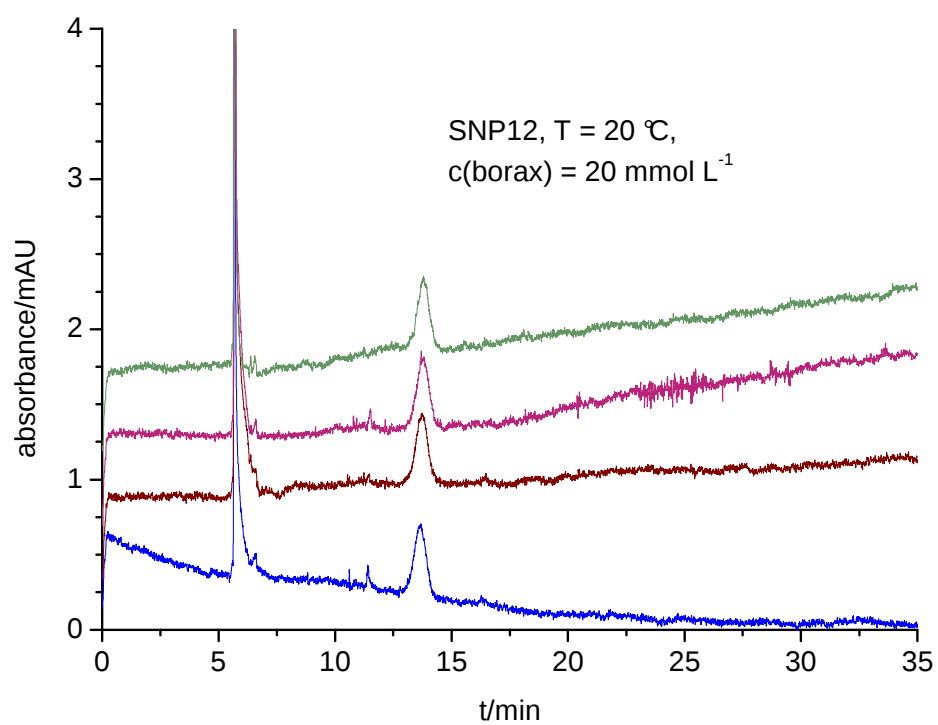
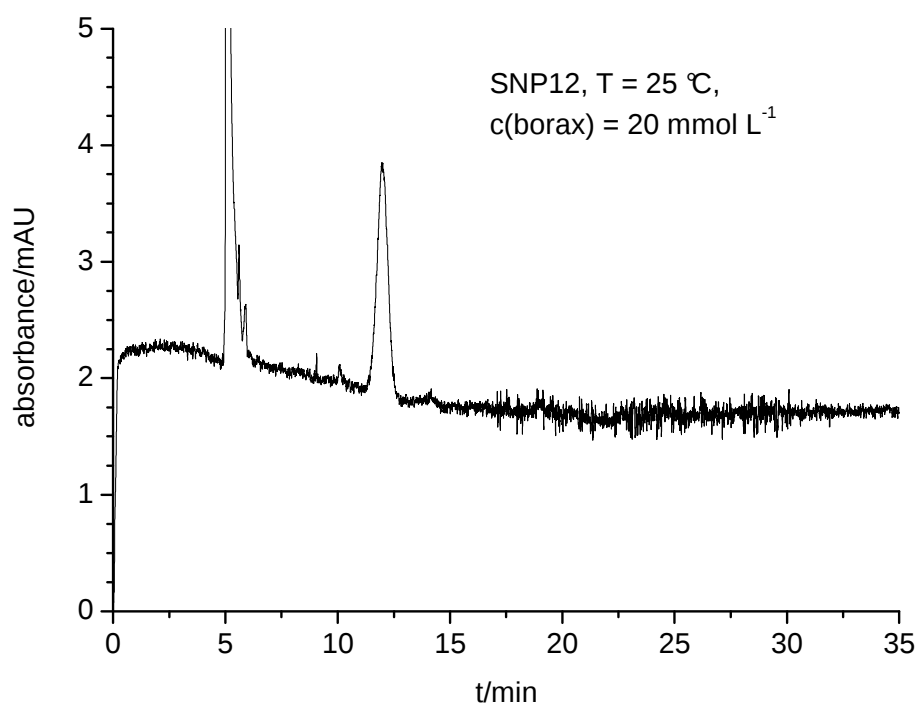
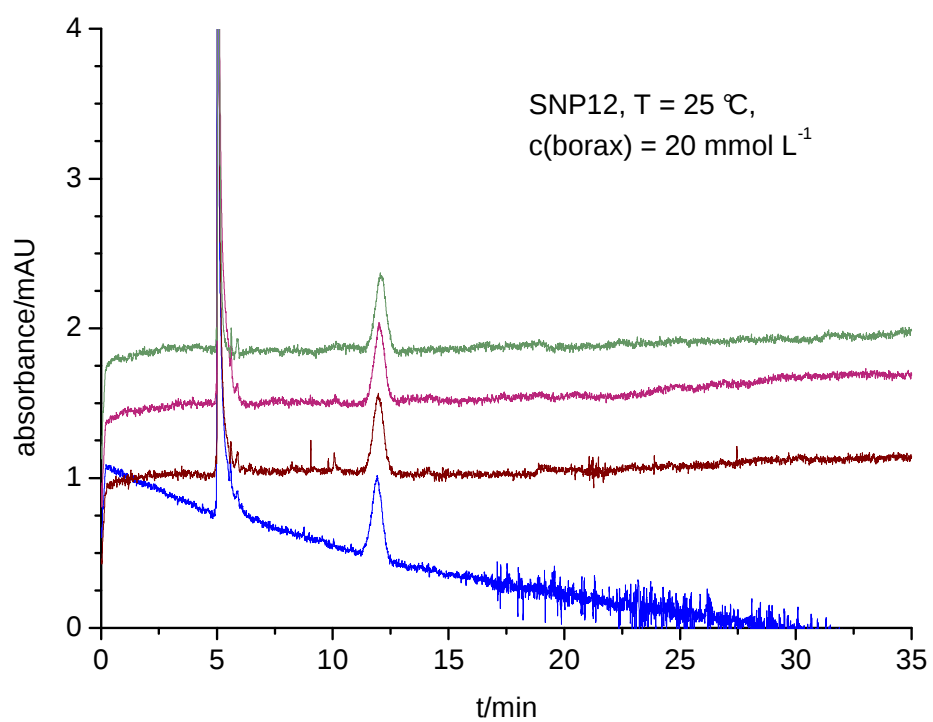
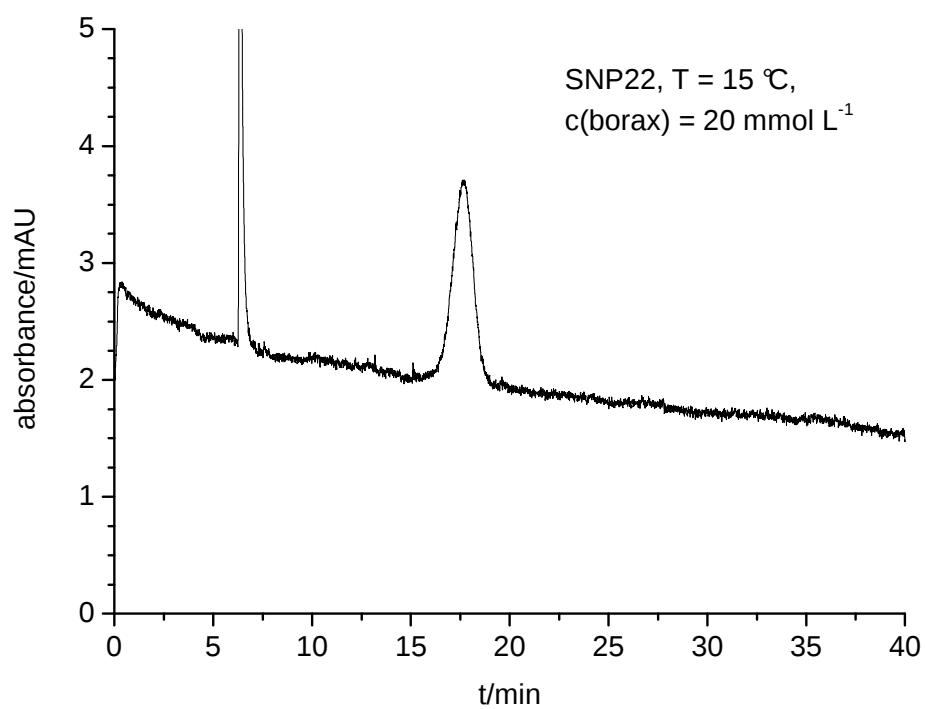
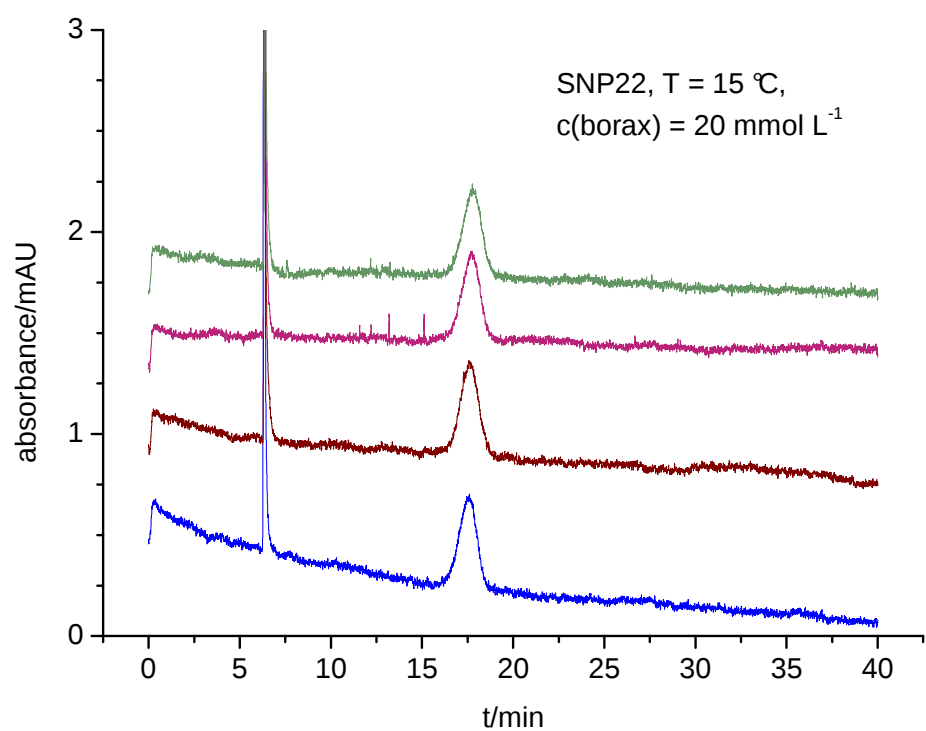


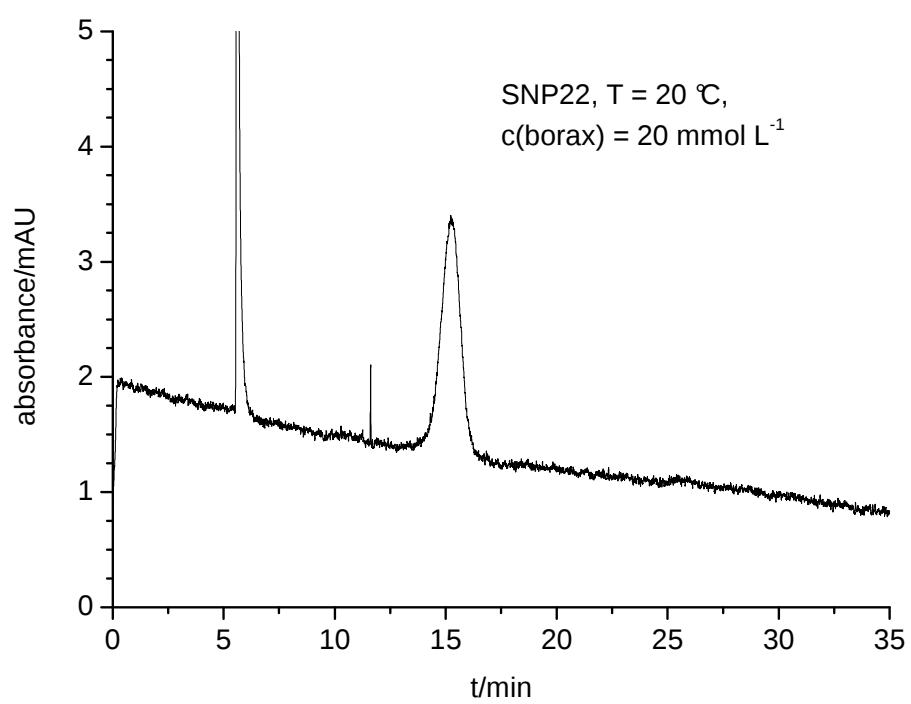
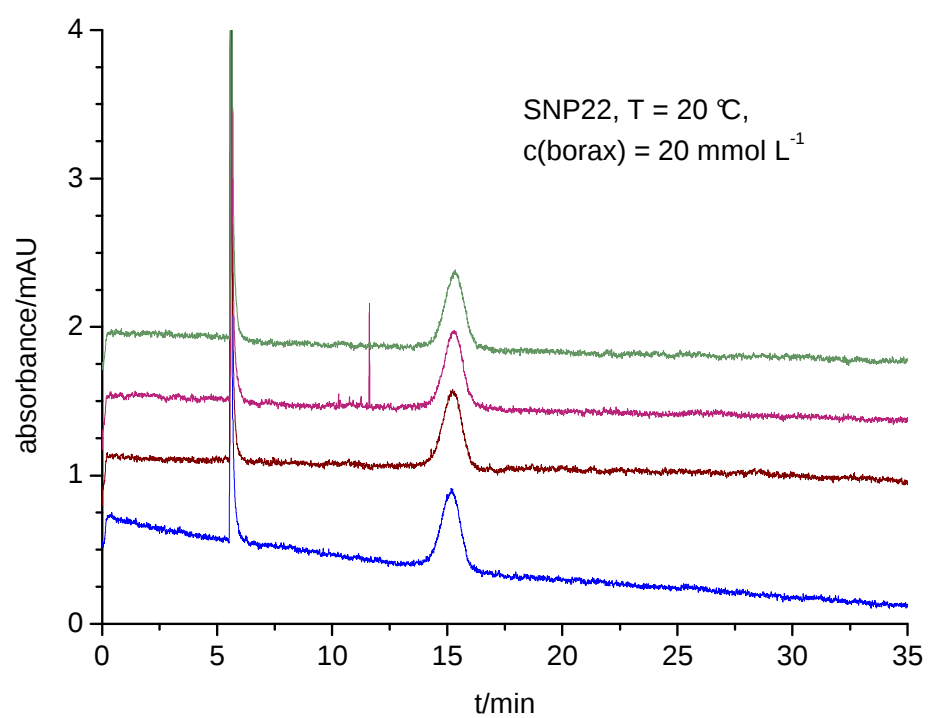
Figure S8. Electropherograms obtained for SNP22 with reduced injection volume: (a) superposition of consecutive runs (sample injection 0.1 psi (6.89 mbar) 3 s, moving average 16 points), (b) cumulative superposition (sample injection 0.1 psi (6.89 mbar) 3 s, , moving average 16 points), (c) superimposed smoothed cumulative curves (Savitzky-Golay algorithm 500 points) fitted to Gram-Charlier series of type A (upper curve: sample injection 0.1 psi (6.89 mbar) 6 s, lower curve: sample injection 0.1 psi (6.89 mbar) 3 s). Experimental conditions: $T = 20\text{ }^{\circ}\text{C}$, total length of capillary = 395 mm, capillary length to detector = 292 mm, inner diameter of fused silica capillary = $75\text{ }\mu\text{m}$, separation electrolyte 30 mmol L^{-1} borax in water ($\text{pH} = 9.2$), separation voltage 7 kV, data rate 16 Hz, absorbance detection 214 nm.

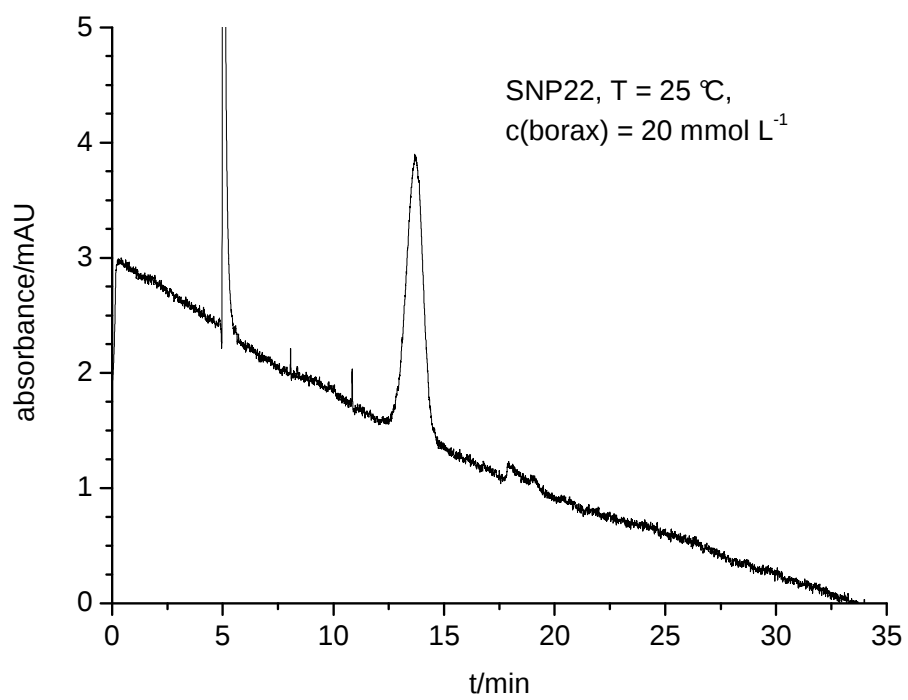
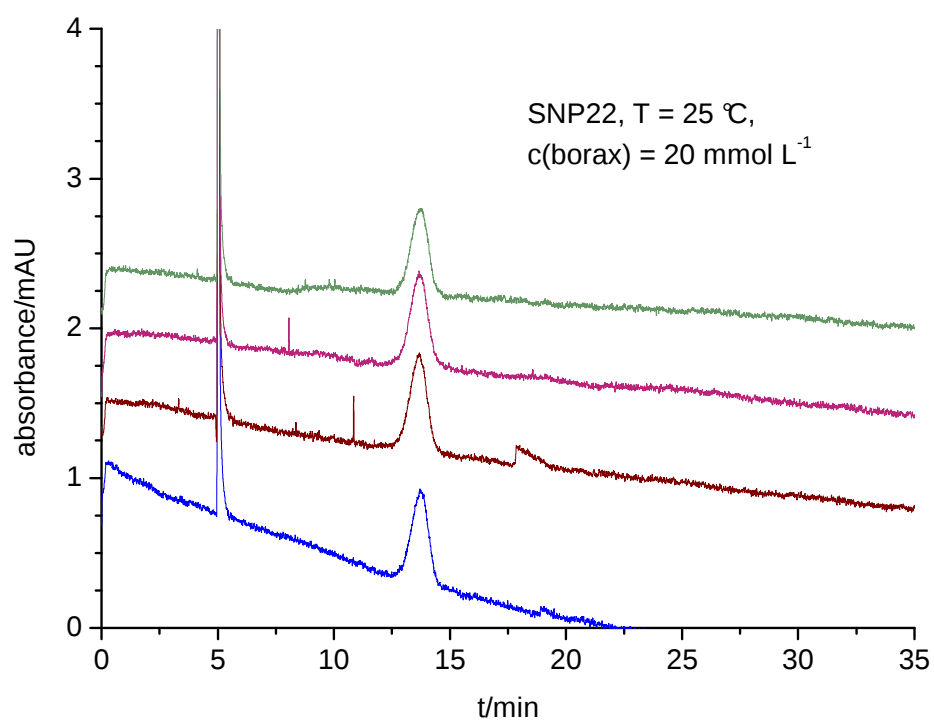


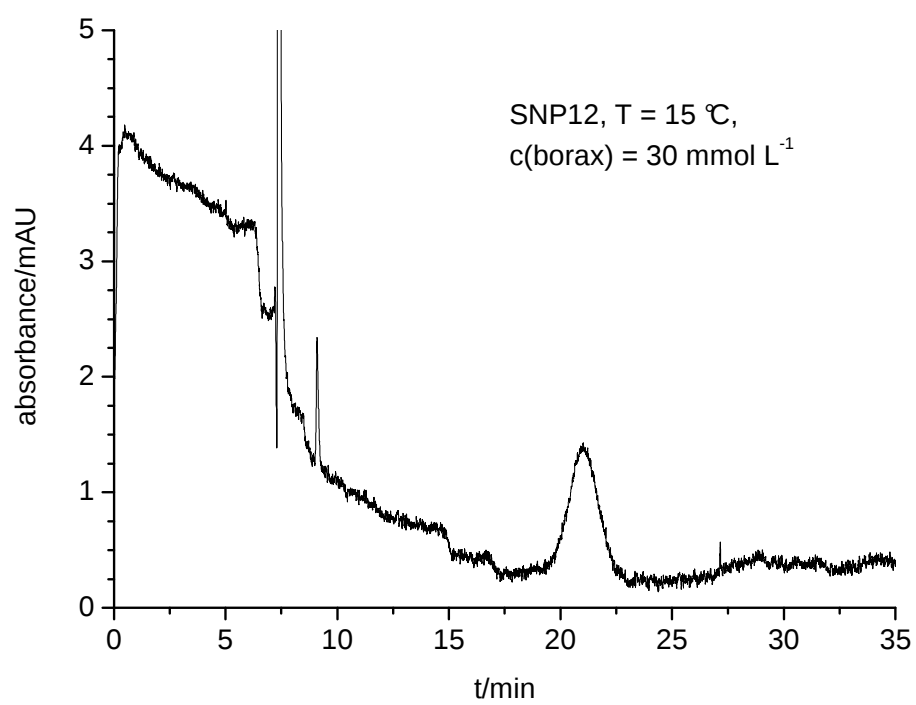
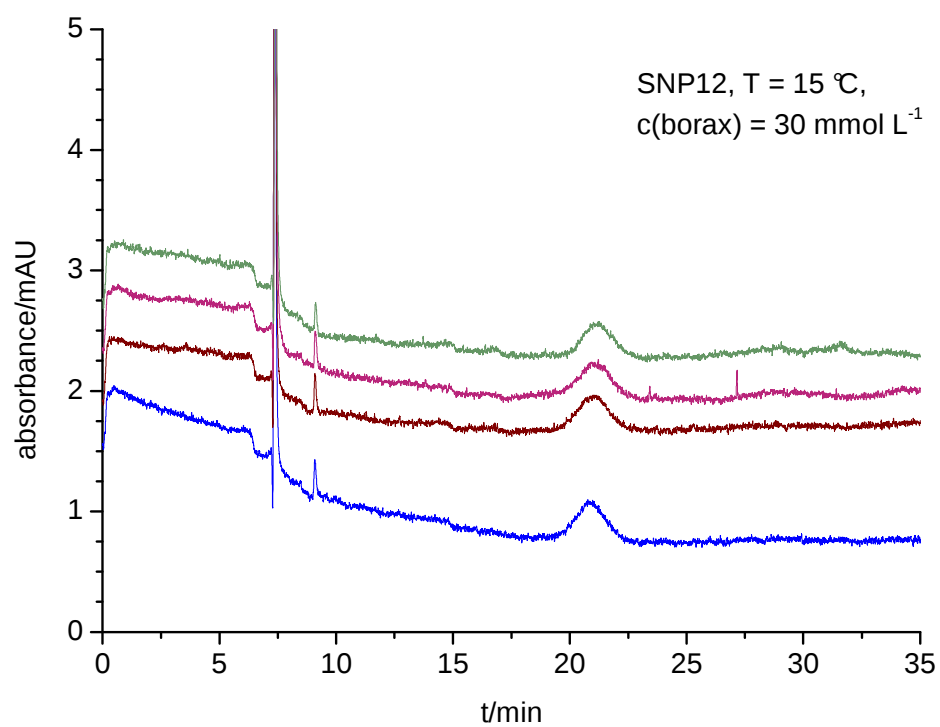


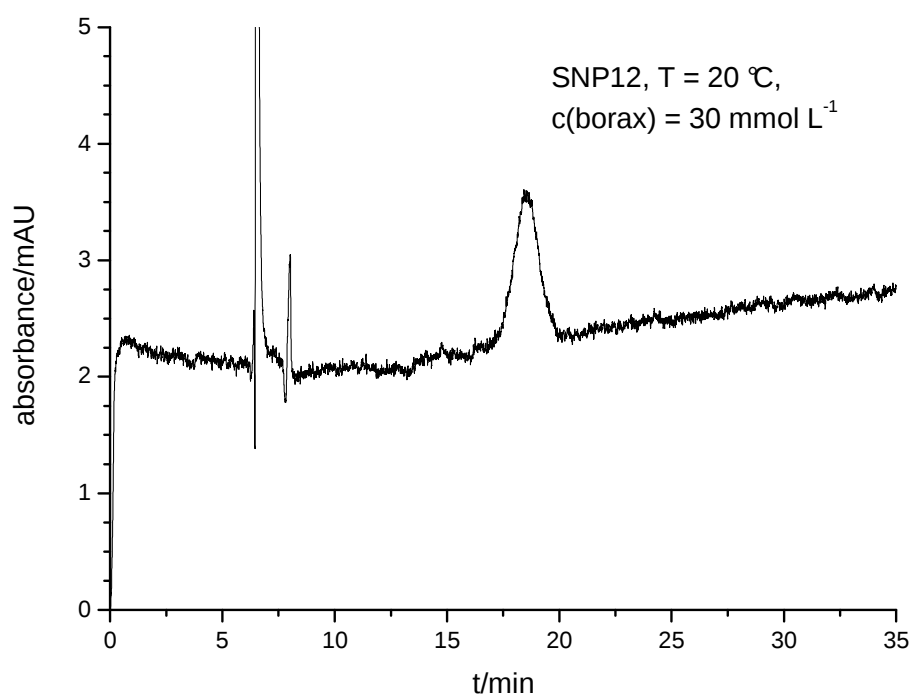
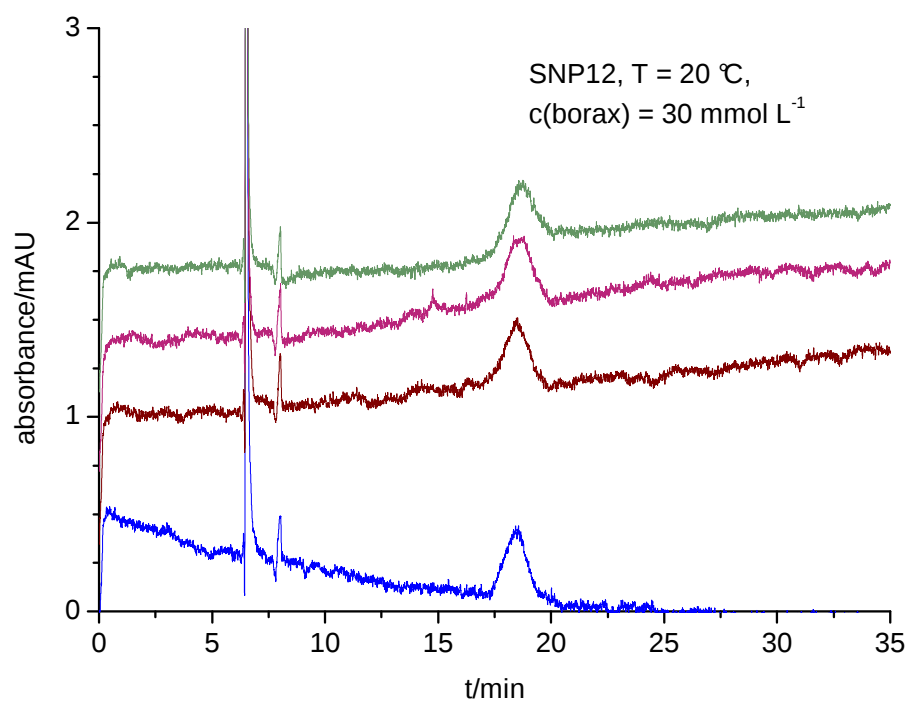


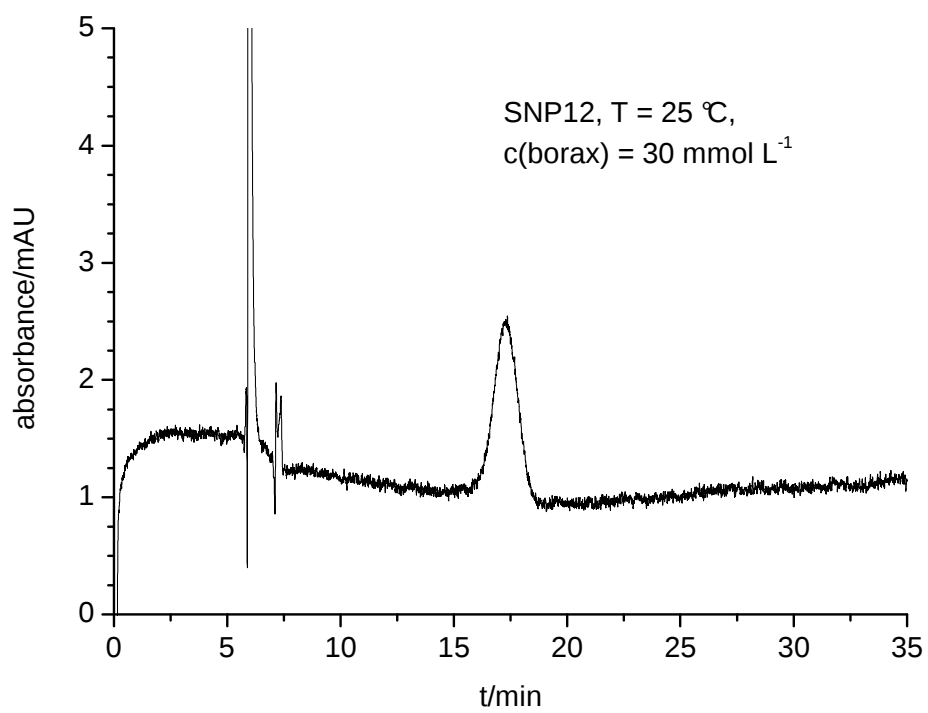
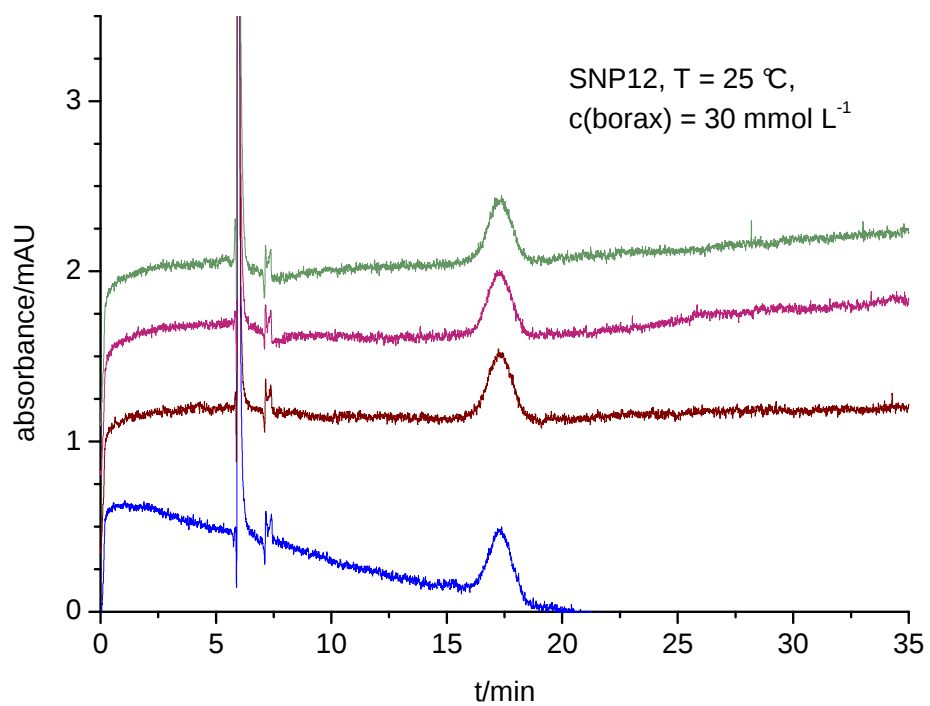


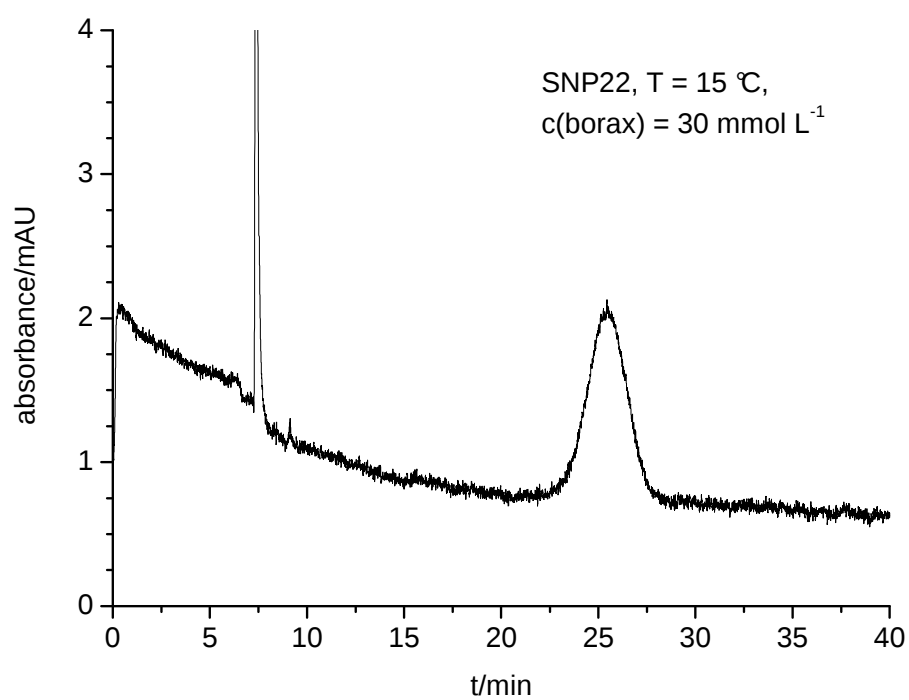
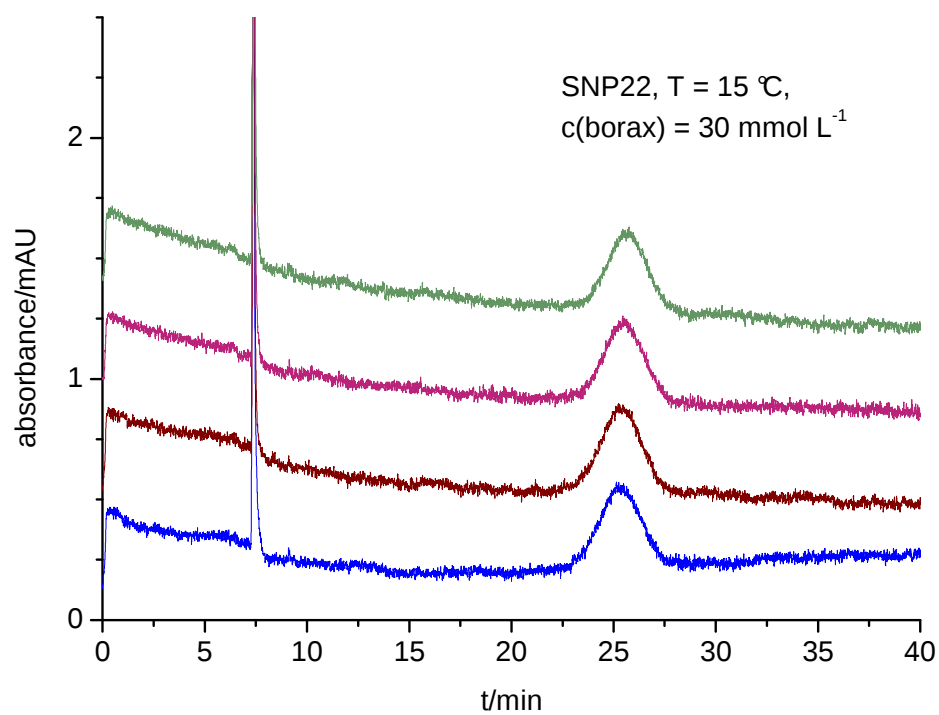


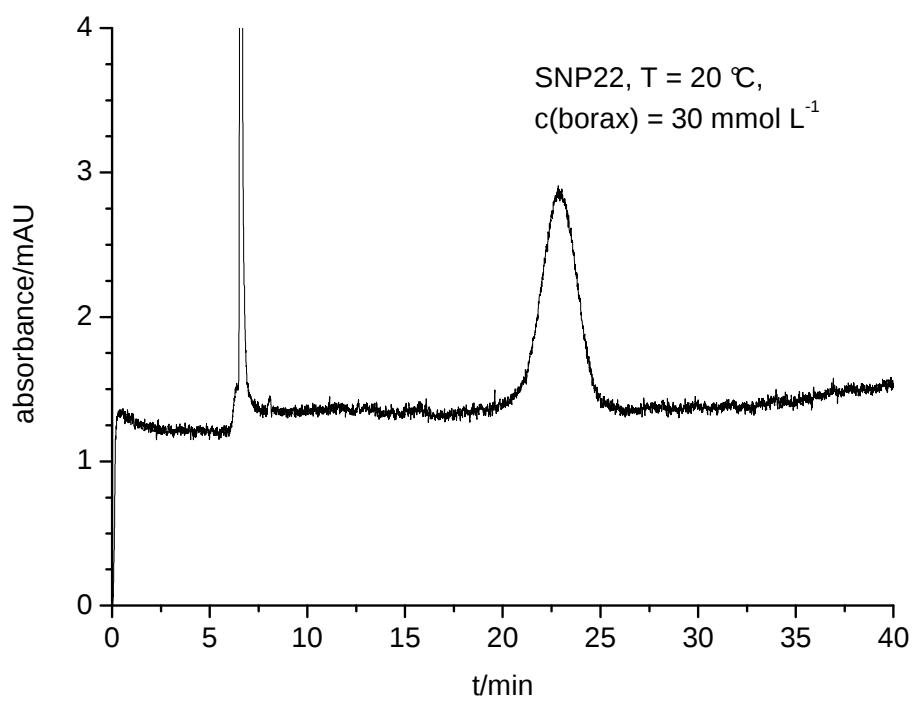
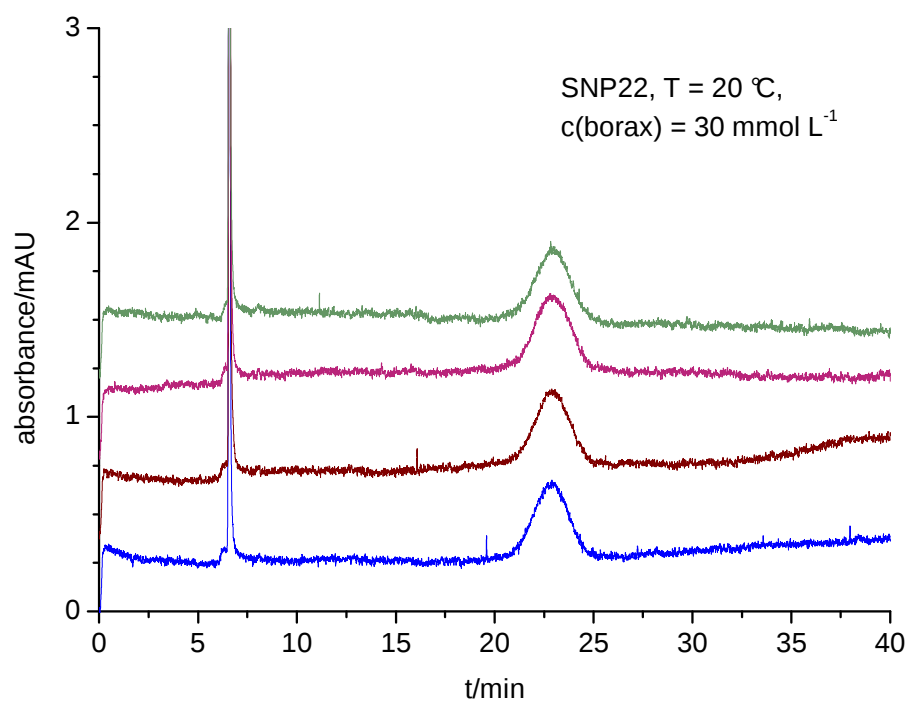


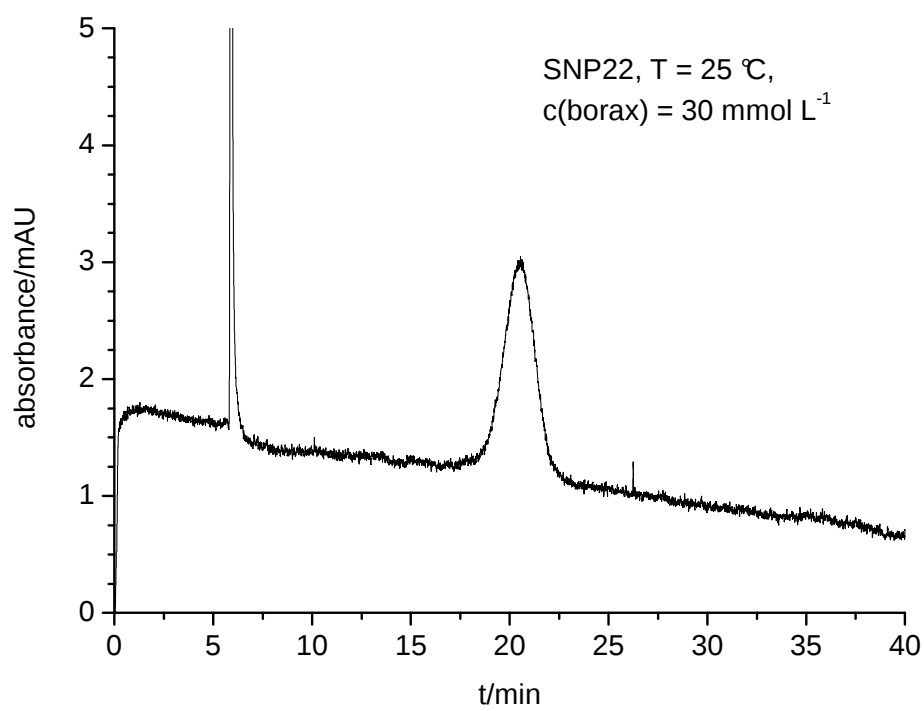
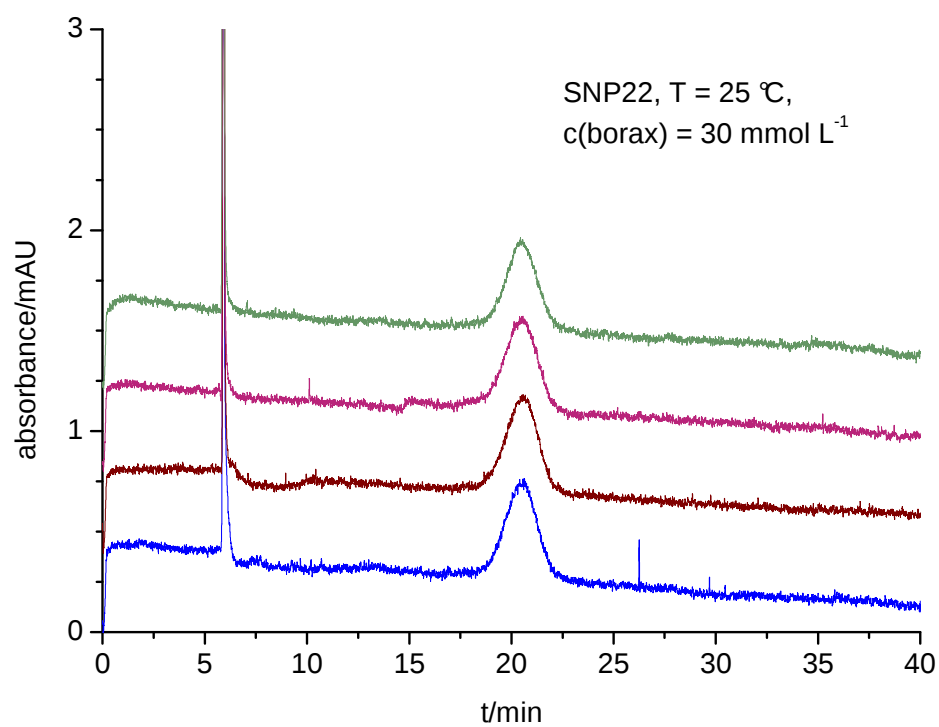


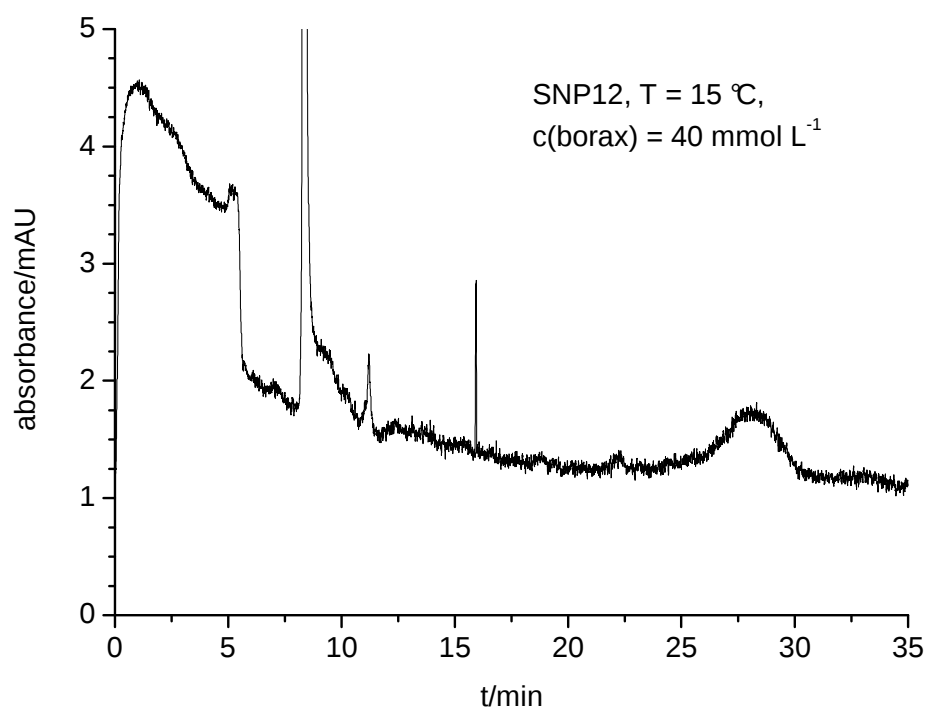
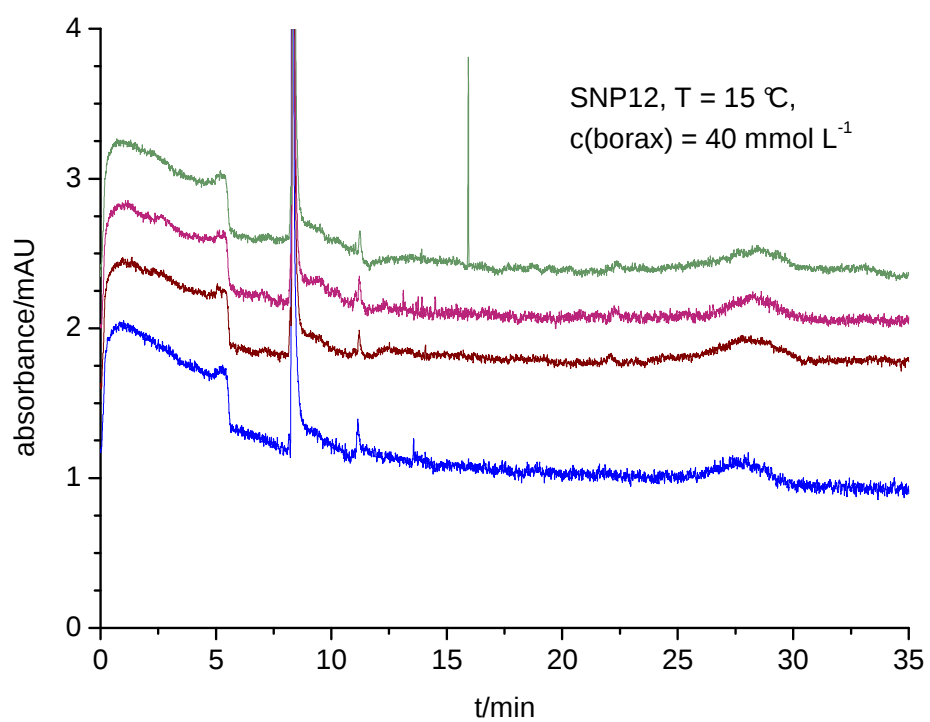


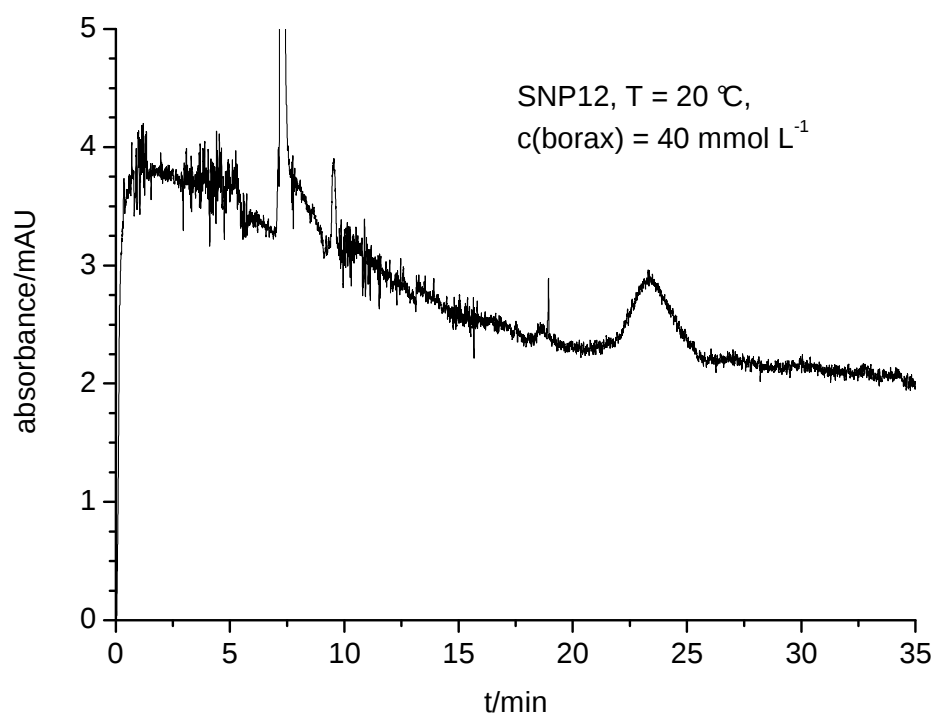
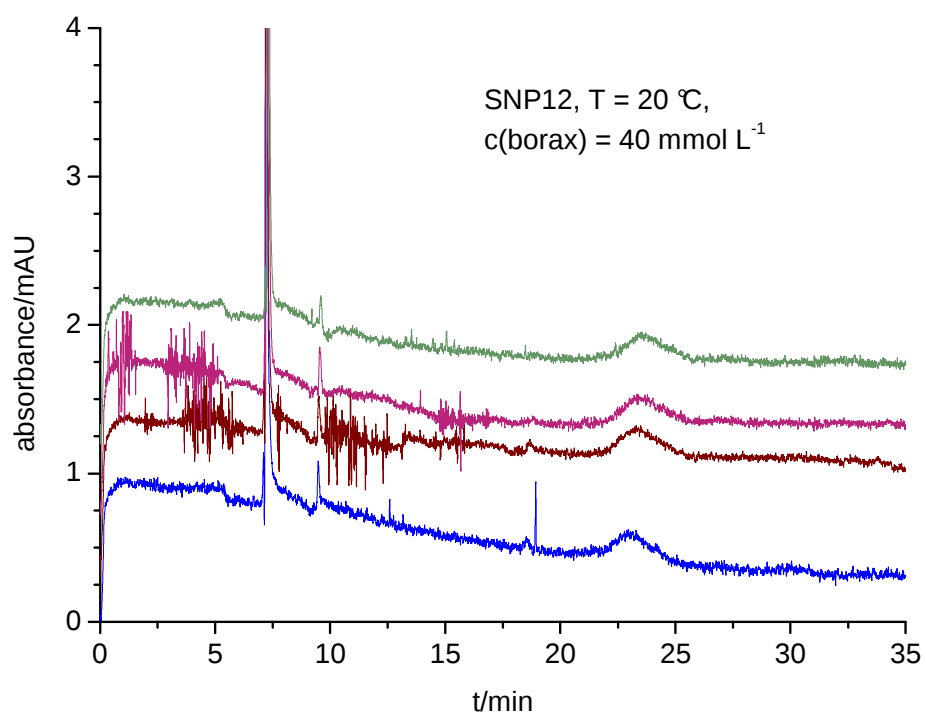


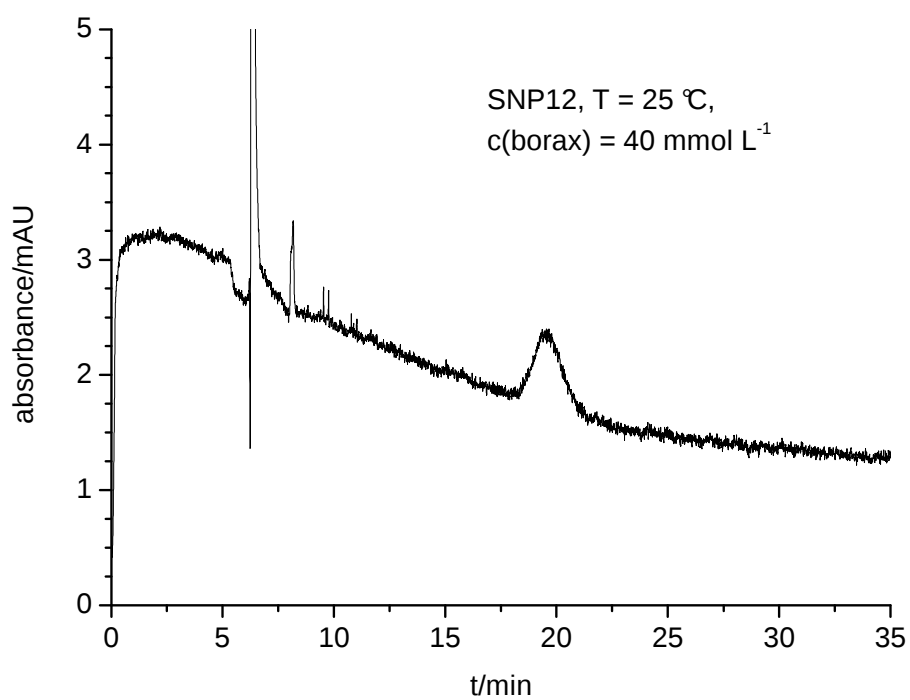
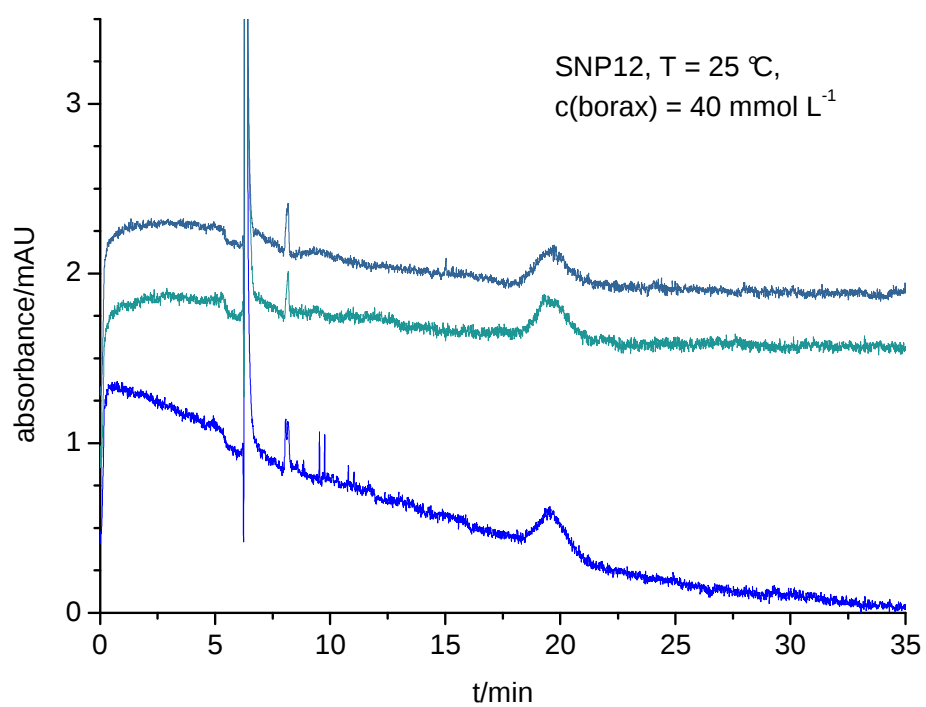


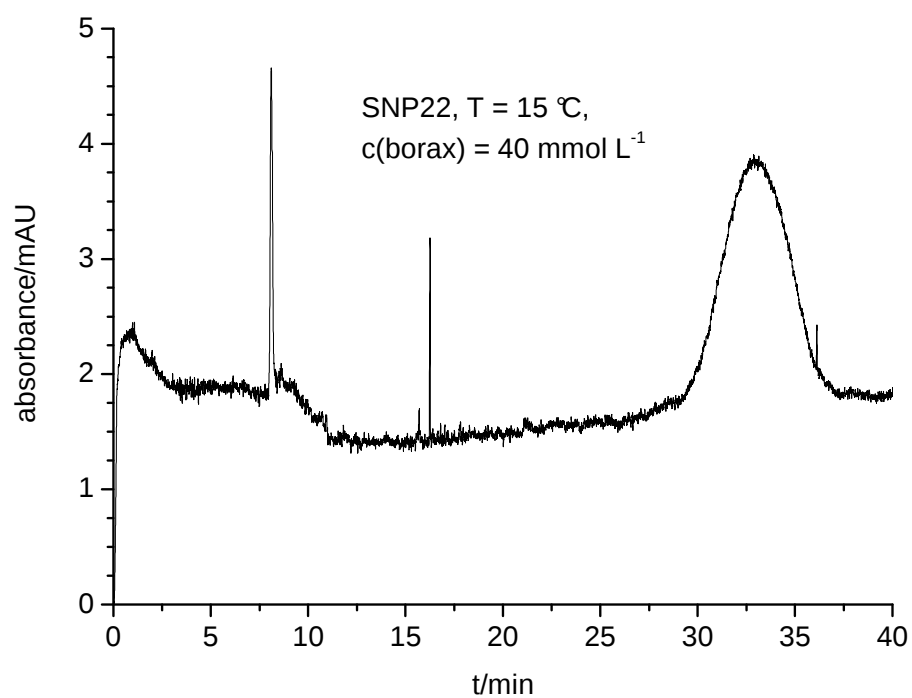
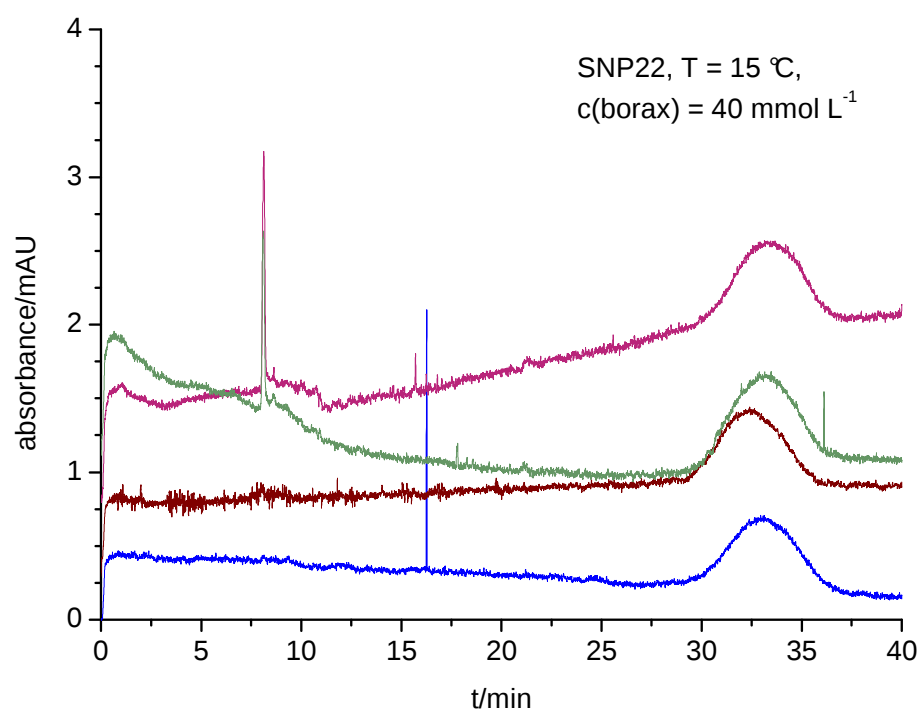


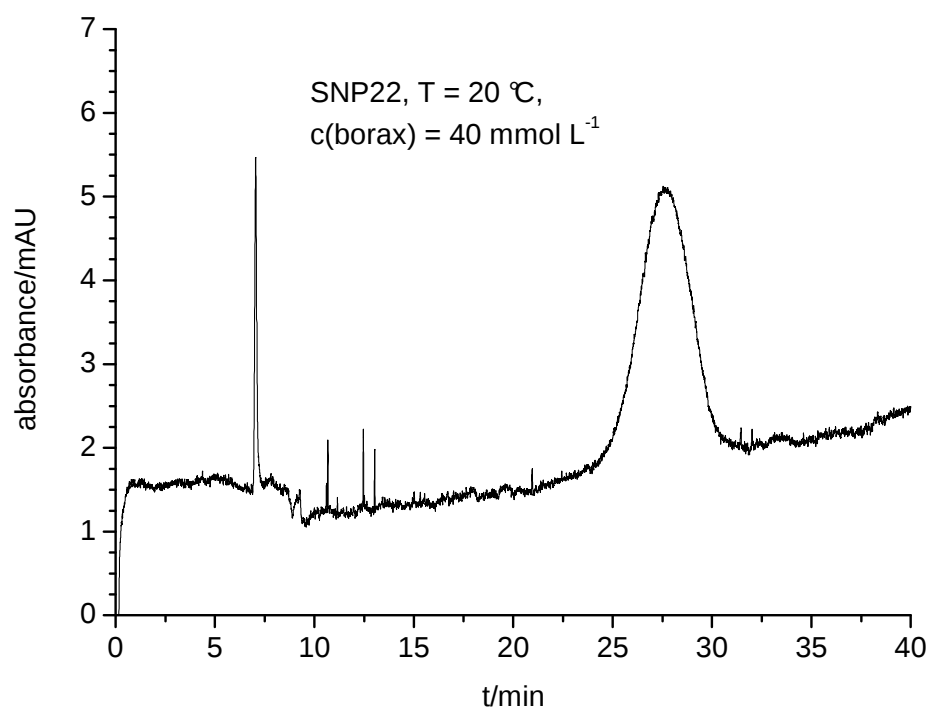
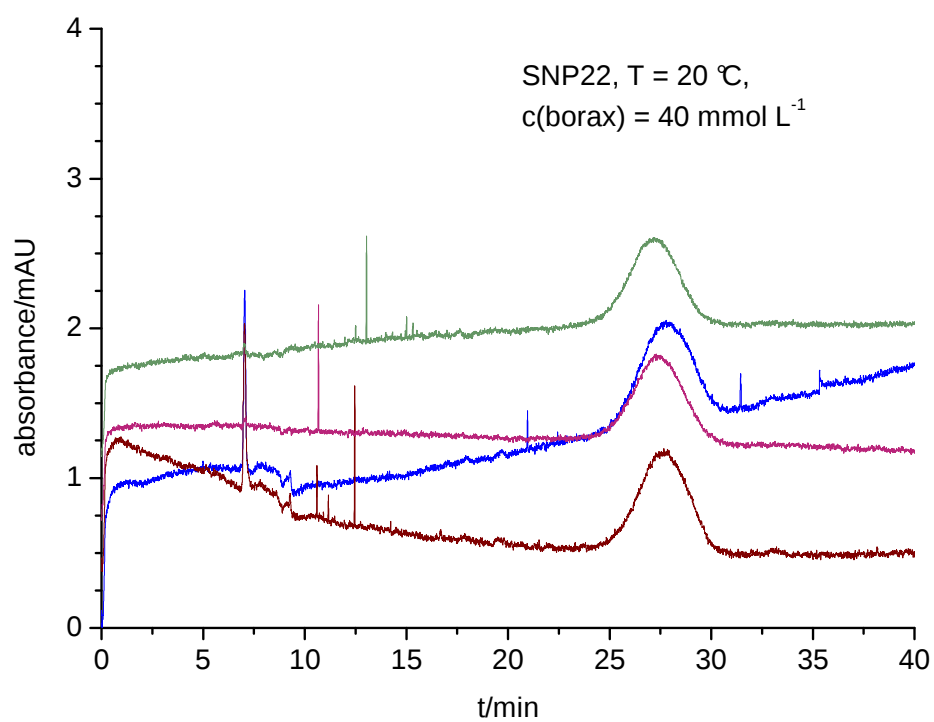


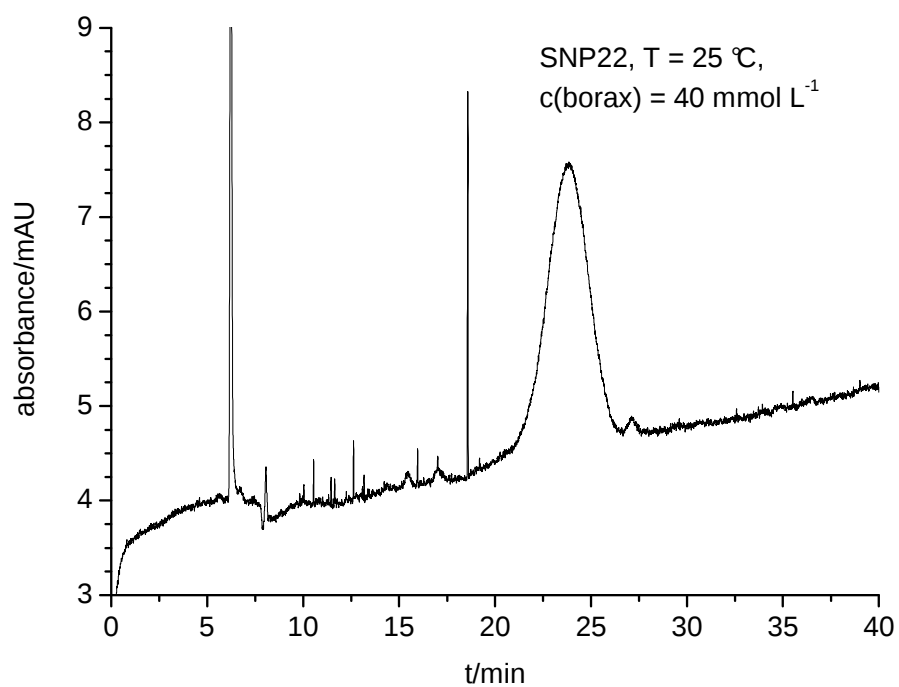
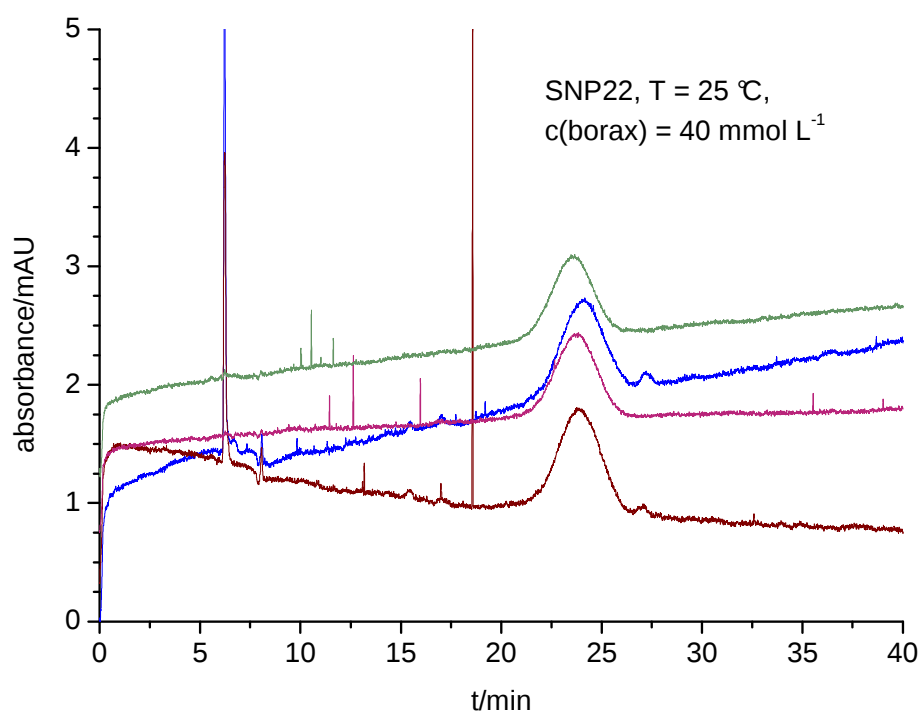


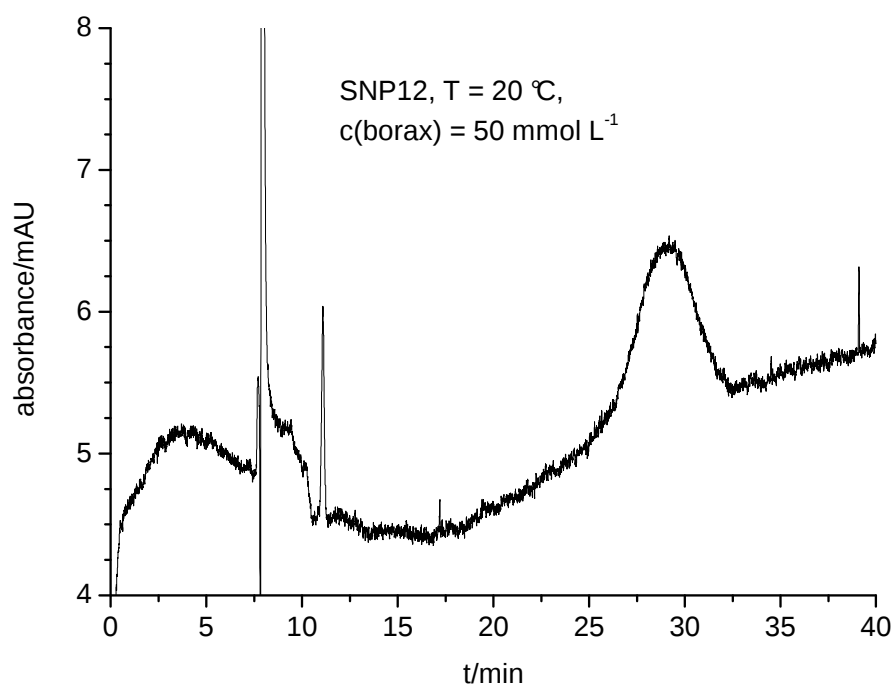
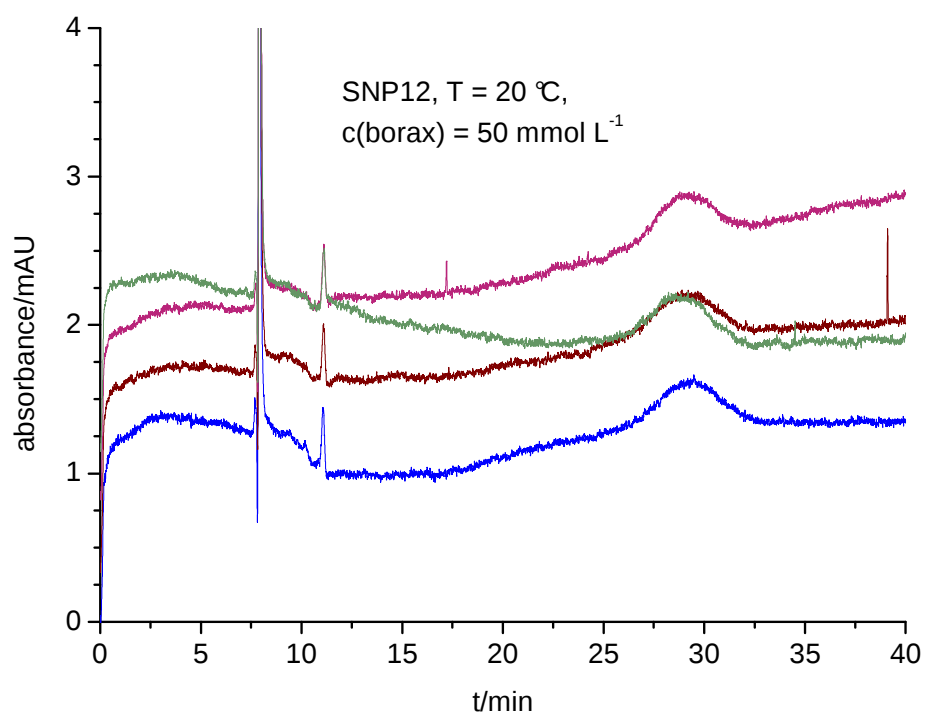


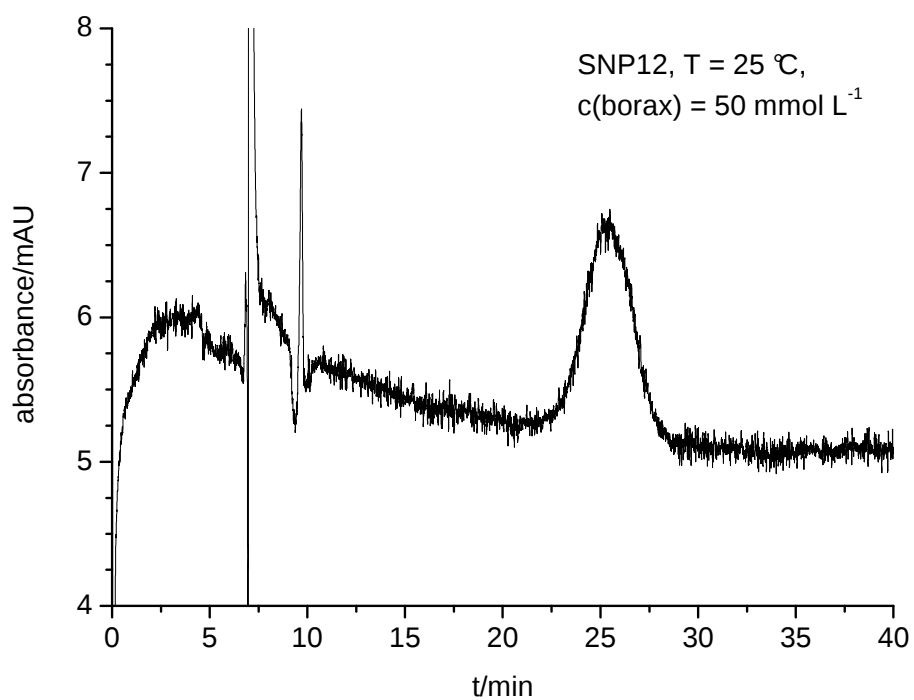
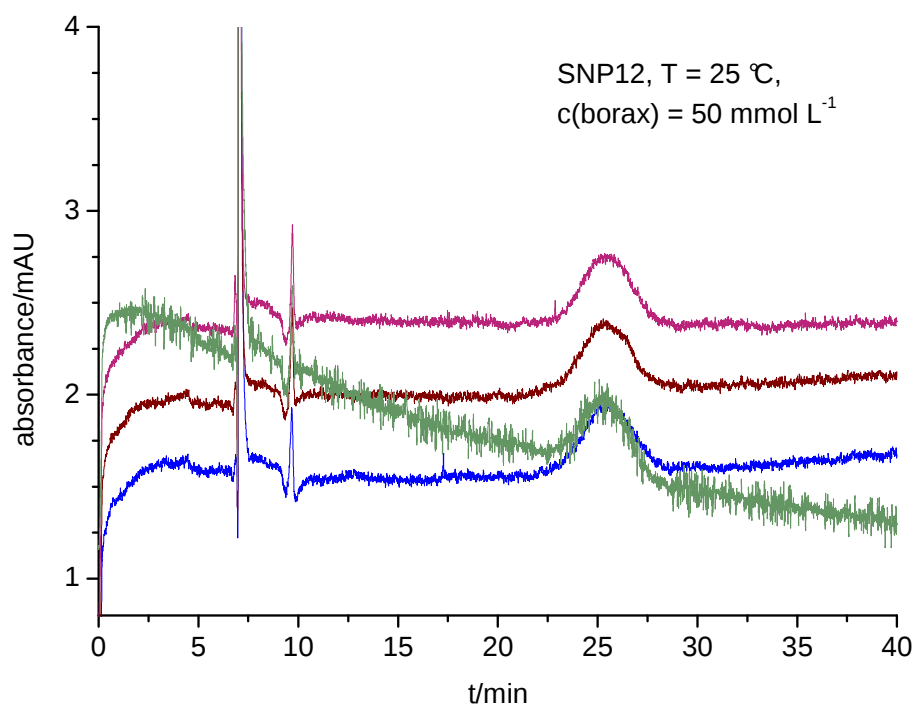


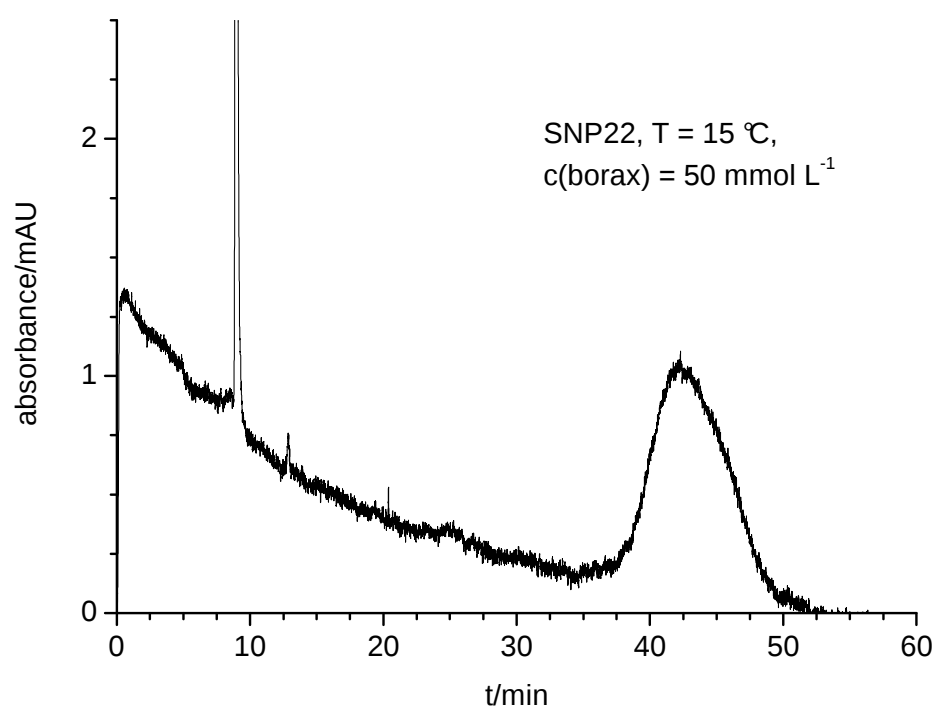
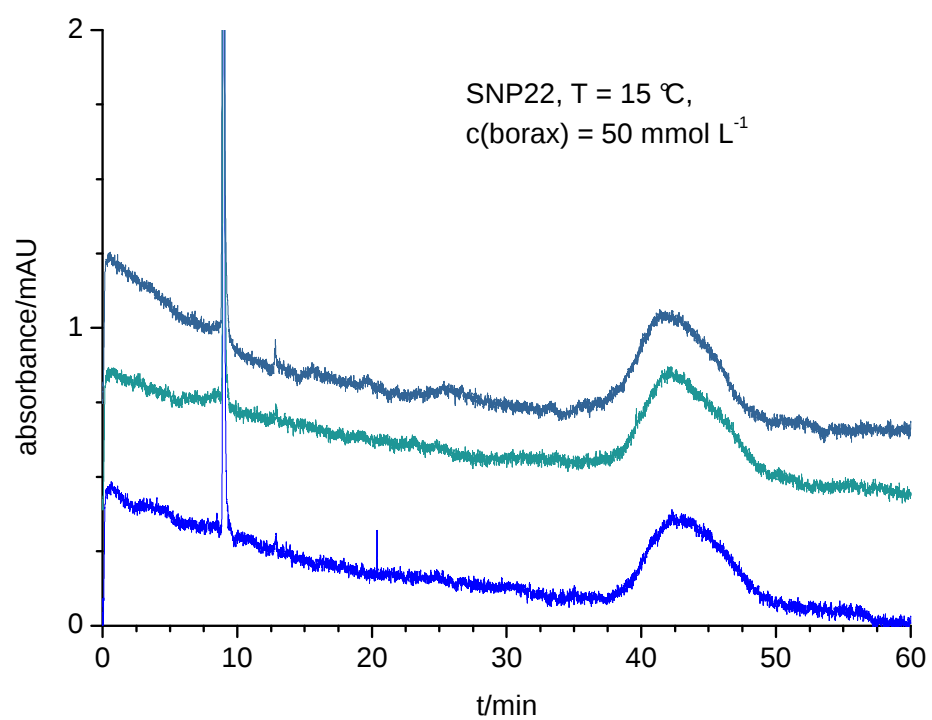


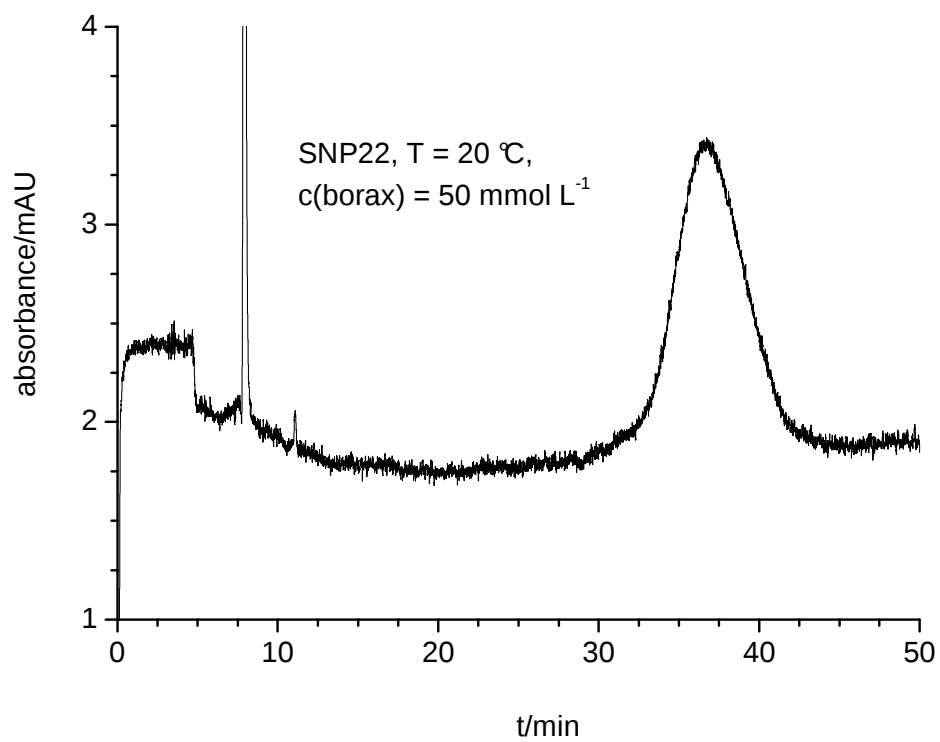
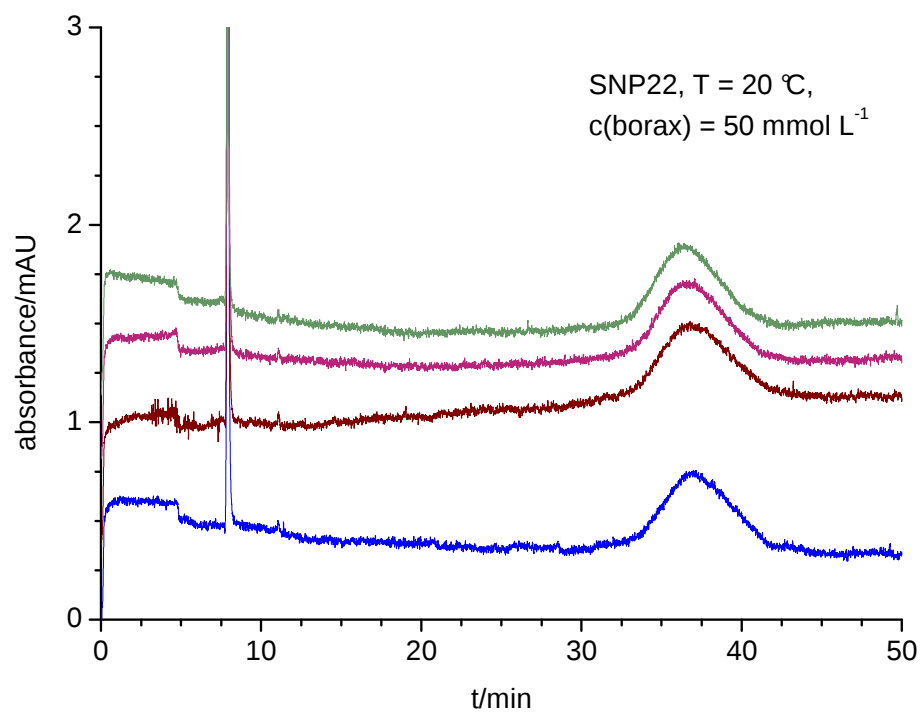


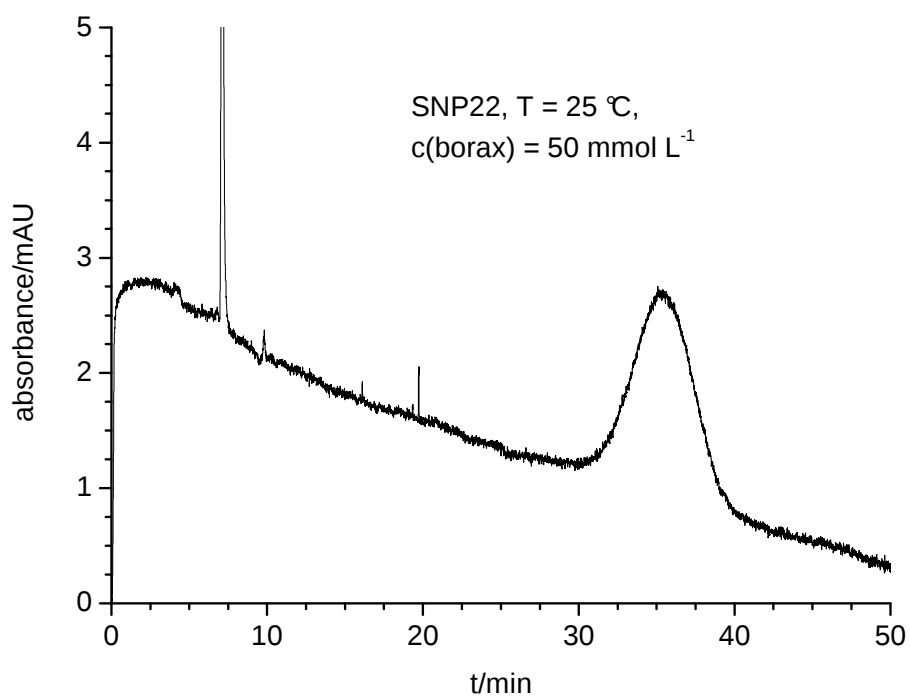
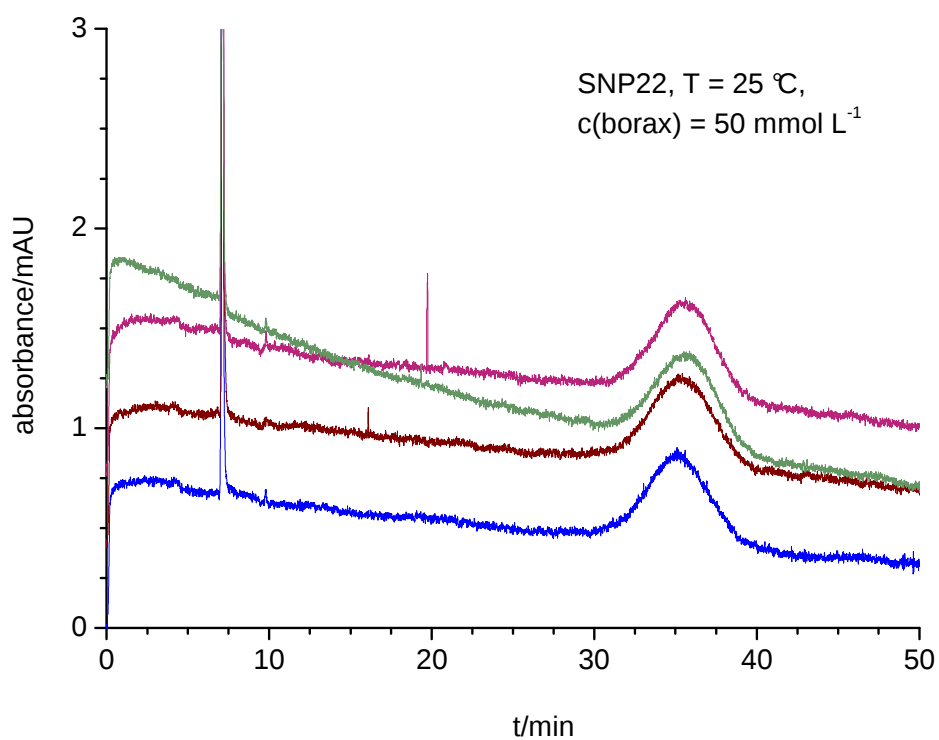


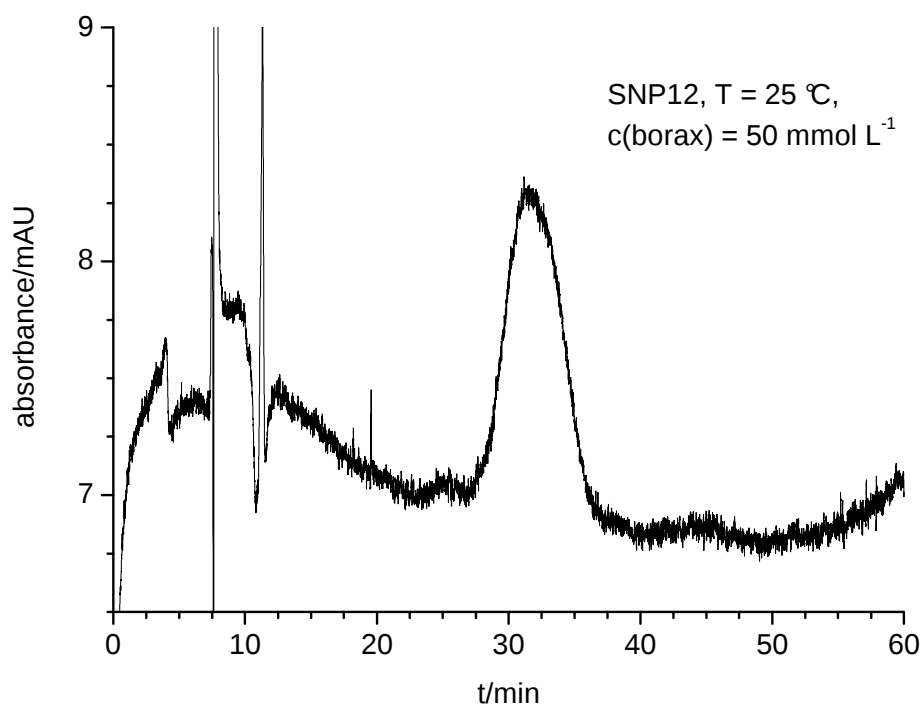
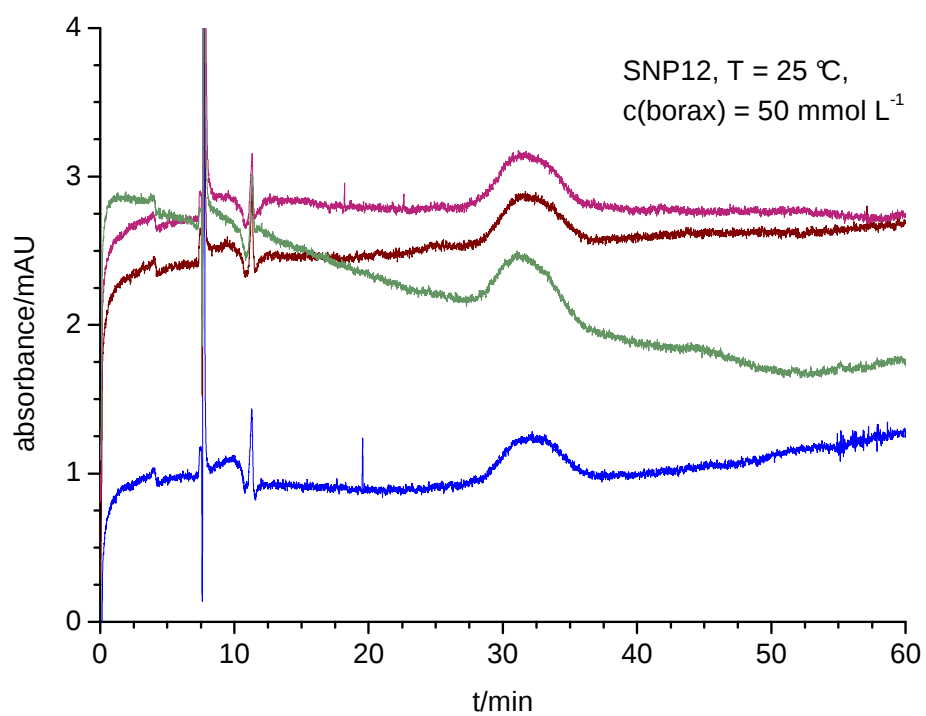


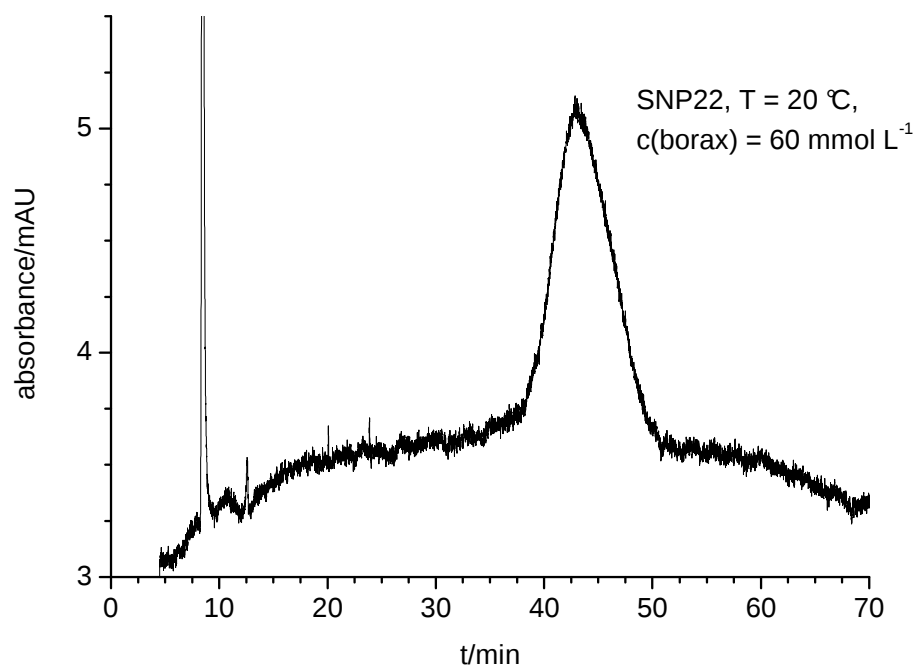
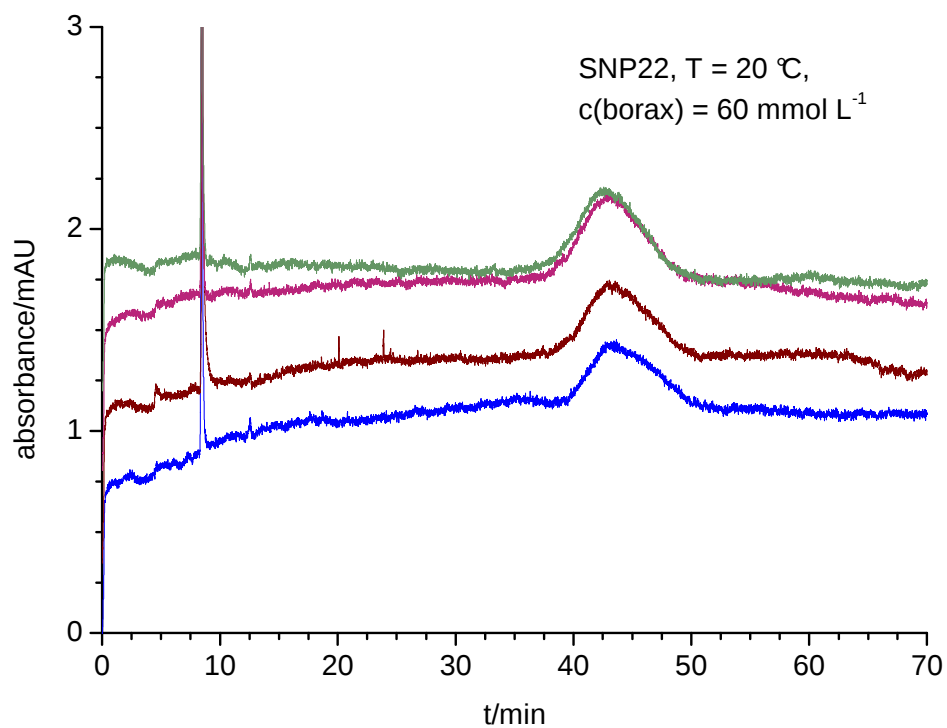












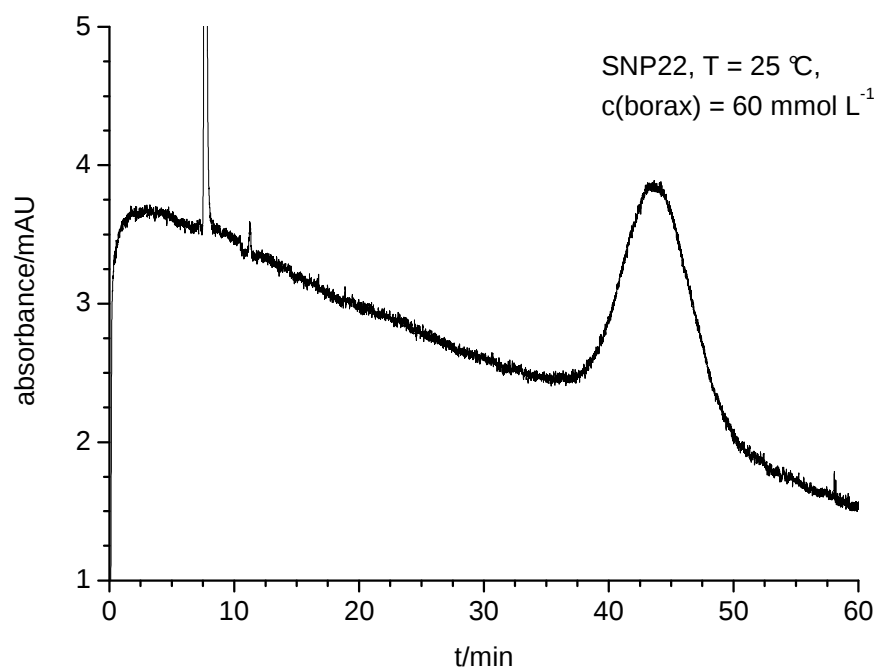
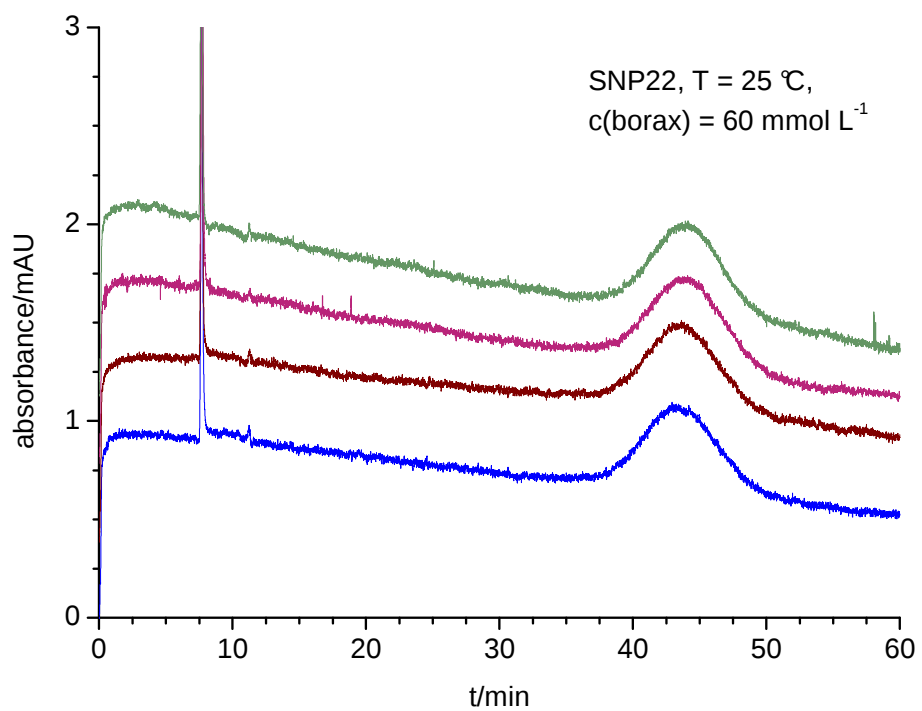
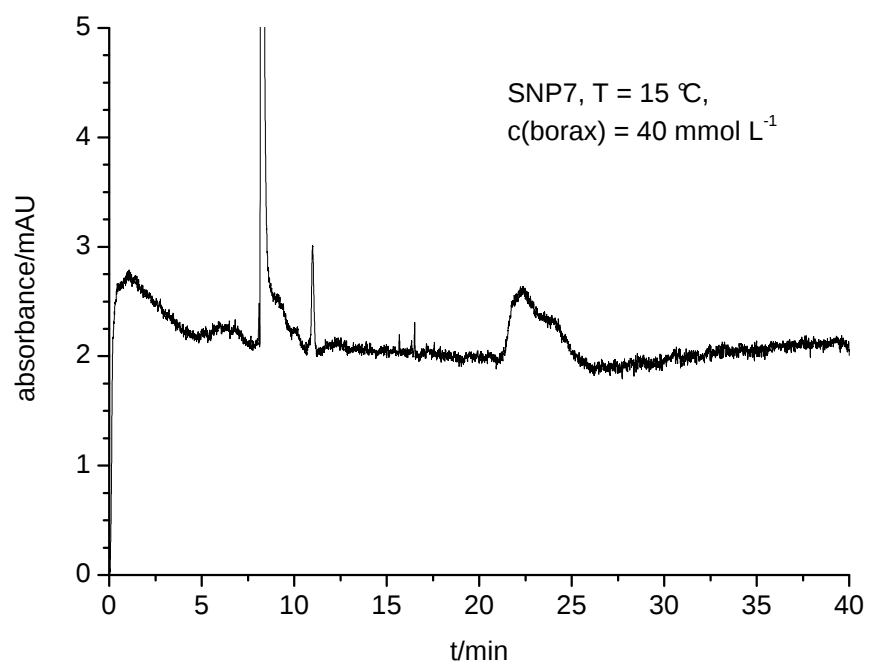
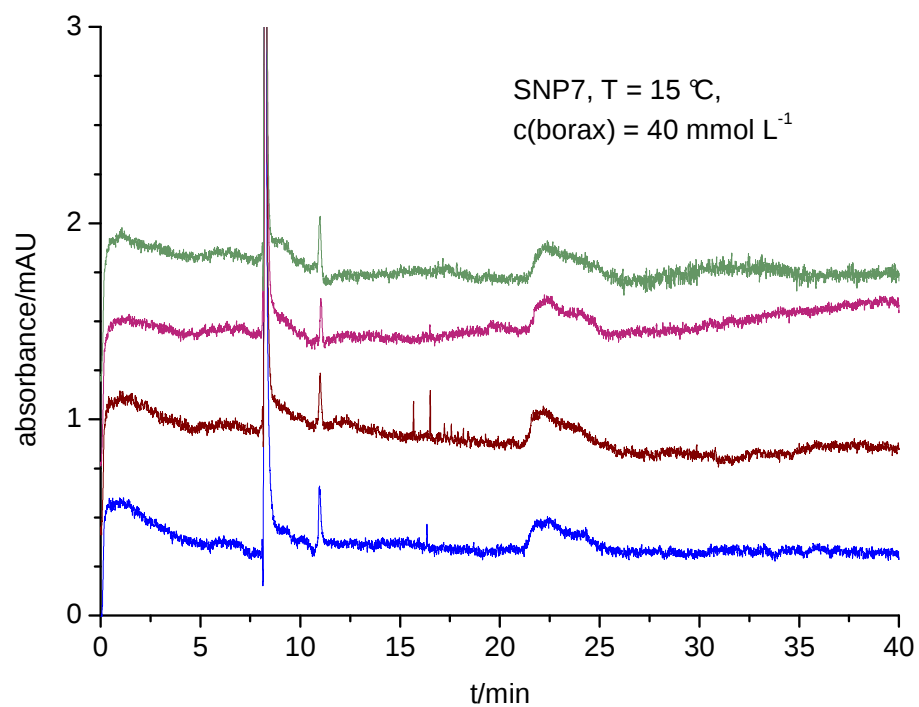
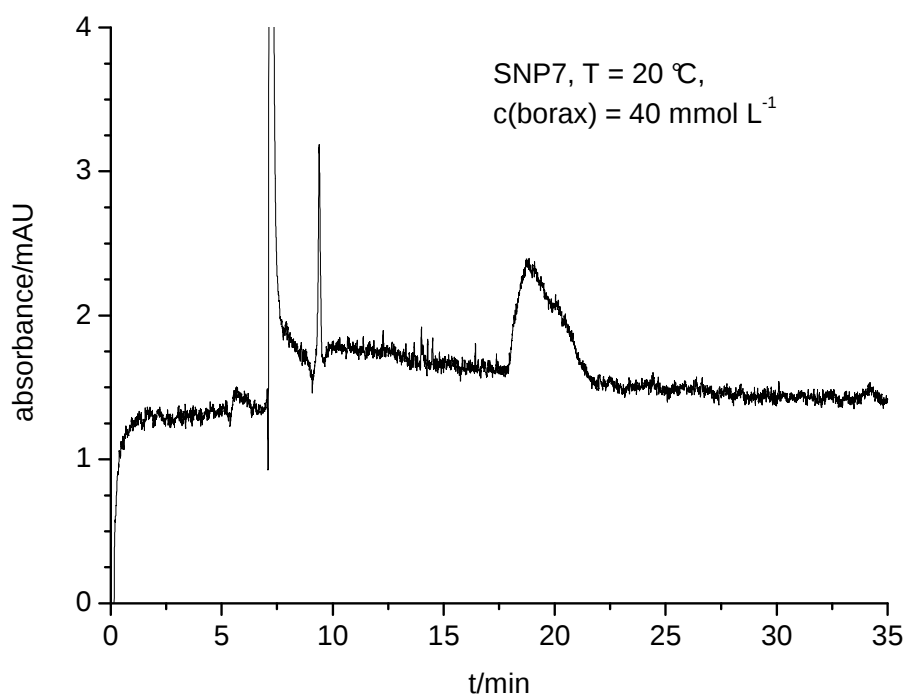
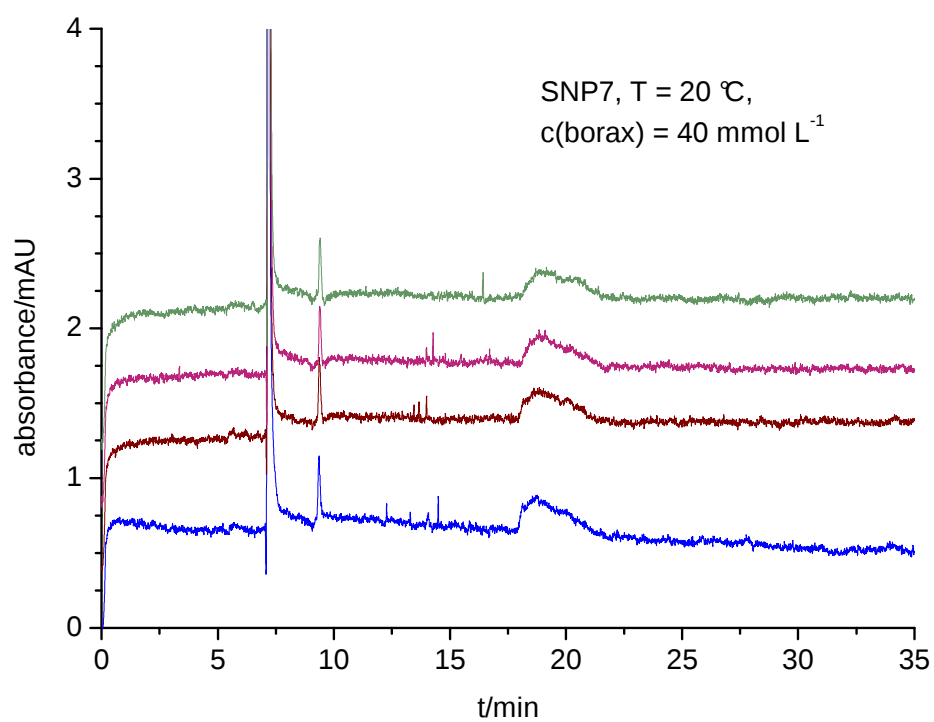
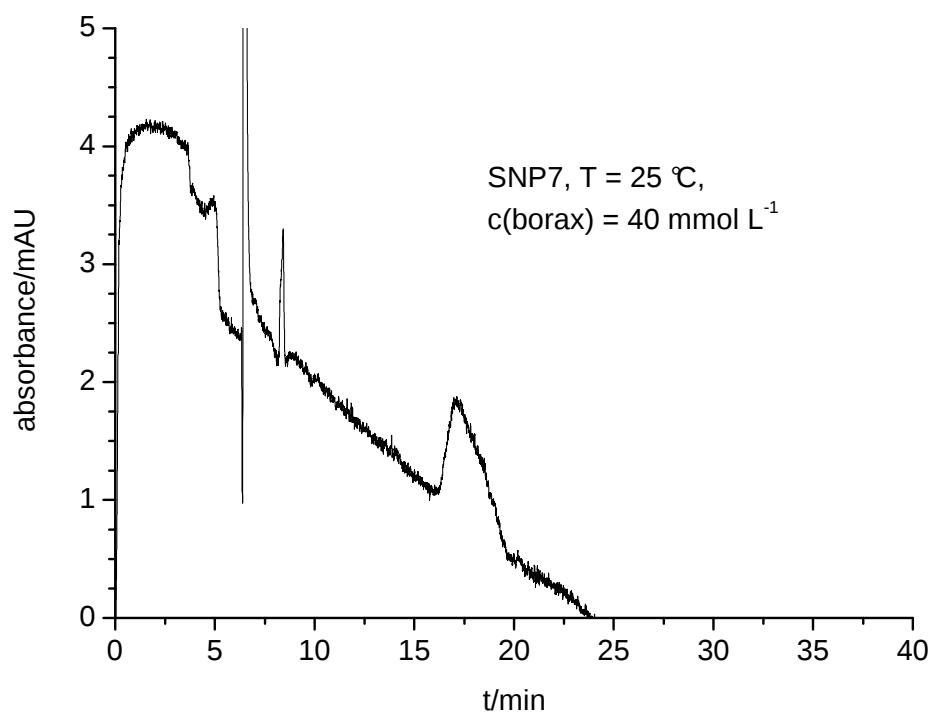
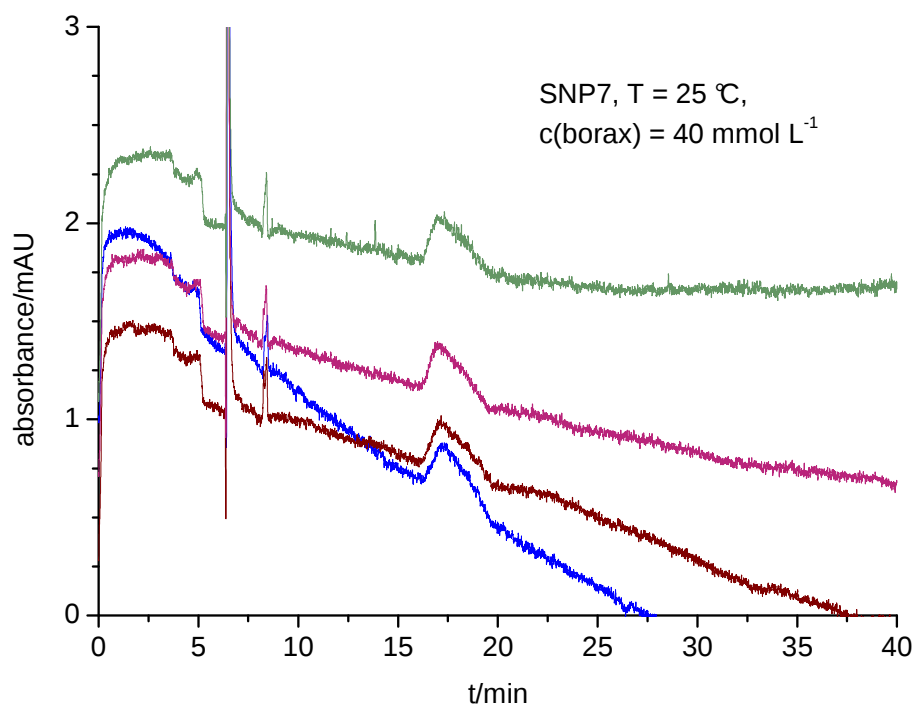
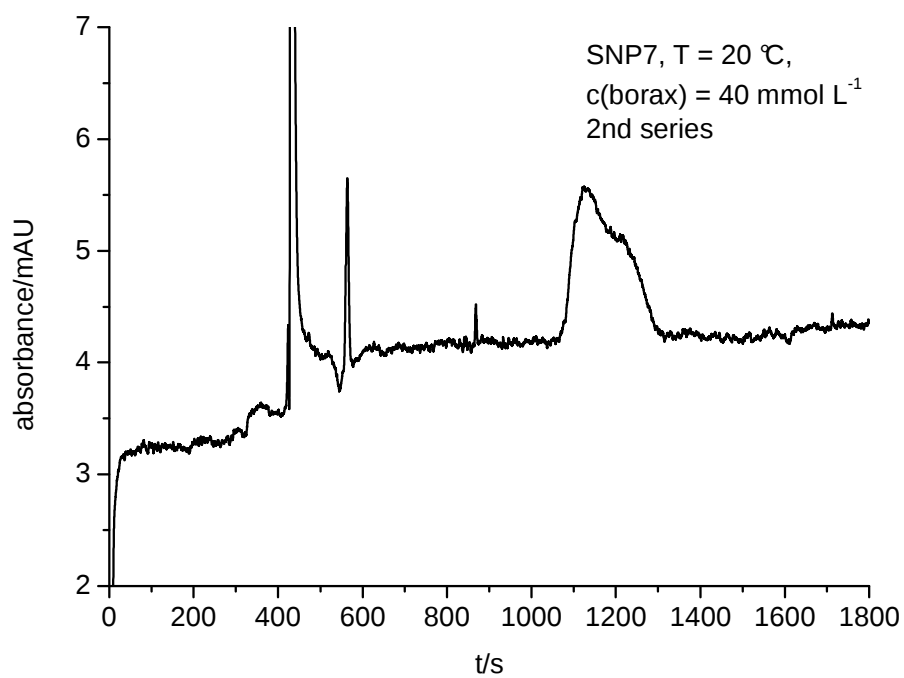
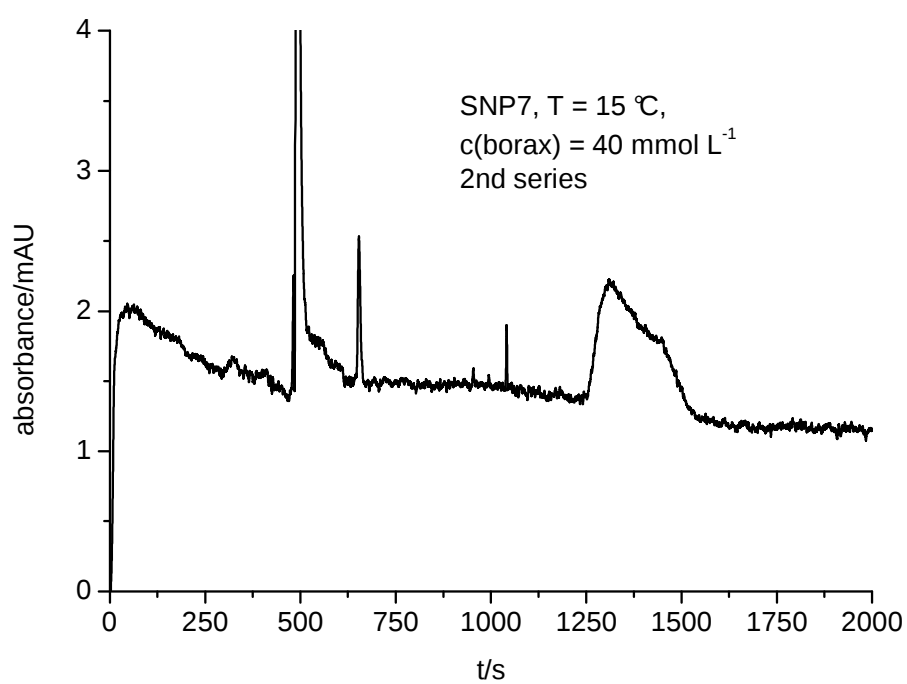


Figure S9. For SNP12 and SNP22 comparison of superimposed electropherograms obtained in consecutive runs (colored lines) with electropherogram calculated from added traces (black line). Experimental conditions: T see figure inset, total length of capillary = 395 mm, capillary length to detector = 292 mm, inner diameter of fused silica capillary = 75 μm , separation electrolyte borax in water (pH = 9.2), separation voltage 7 kV, data rate 16 Hz (moving average 16 points), absorbance detection 200 nm (SNP12) or 214 nm (SNP22). Sample injection parameters: (a, SNP12, $c(\text{borax}) = 20 \text{ mmol L}^{-1}$) 0.2 psi (13.78 mbar) 6 s, (b, SNP22, $c(\text{borax}) = 20 \text{ mmol L}^{-1}$) 0.1 psi (6.89 mbar) 6 s, (c, SNP12, $c(\text{borax}) = 30 \text{ mmol L}^{-1}$) 0.2 psi (13.78 mbar) 6 s, (d, SNP22, $c(\text{borax}) = 30 \text{ mmol L}^{-1}$) 0.1 psi (6.89 mbar) 6 s, (e, SNP12, $c(\text{borax}) = 40 \text{ mmol L}^{-1}$) 0.2 psi (13.78 mbar) 6 s, (f, SNP22, $c(\text{borax}) = 40 \text{ mmol L}^{-1}$) 0.1 psi (6.89 mbar) 6 s, (g, SNP12, $c(\text{borax}) = 50 \text{ mmol L}^{-1}$) 0.2 psi (13.78 mbar) 9 s, (h, SNP22, $c(\text{borax}) = 50 \text{ mmol L}^{-1}$) 0.1 psi (6.89 mbar) 9 s, (i, SNP12, $c(\text{borax}) = 60 \text{ mmol L}^{-1}$) 0.2 psi (13.78 mbar) 12 s, (j, SNP22, $c(\text{borax}) = 60 \text{ mmol L}^{-1}$) 0.2 psi (13.78 mbar) 6 s.









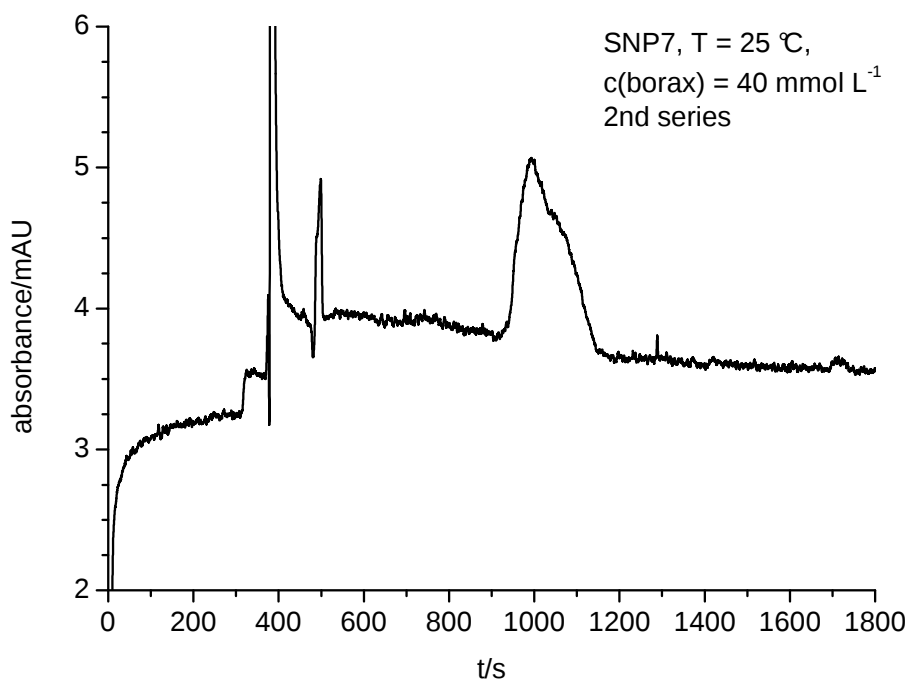


Figure S10. For SNP7 (first series) comparison of superimposed electropherograms obtained in consecutive runs (colored lines) with electropherogram calculated from added traces (black line). Experimental conditions: T see figure inset, total length of capillary = 395 mm, capillary length to detector = 292 mm, inner diameter of fused silica capillary = 75 μm , separation electrolyte borax in water (pH = 9.2), separation voltage 7 kV, data rate 16 Hz (moving average 16 points), absorbance detection 200 nm. Sample injection parameters: (a, first series) 0.1 psi (6.89 mbar) 6 s, (b, second series) 0.2 psi (13.78 mbar) 6 s. Second series: smoothed cumulative superposition of four traces Savitzky Golay algorithm 40 points.

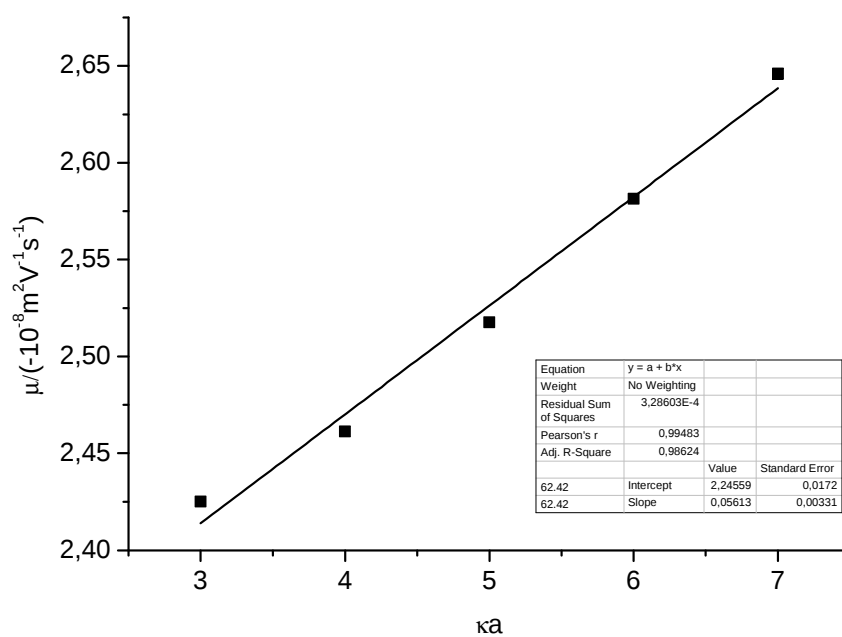


Figure S11a. Regression line for SNP12, T = 15 °C, c(borax) = 20 mmol L⁻¹.

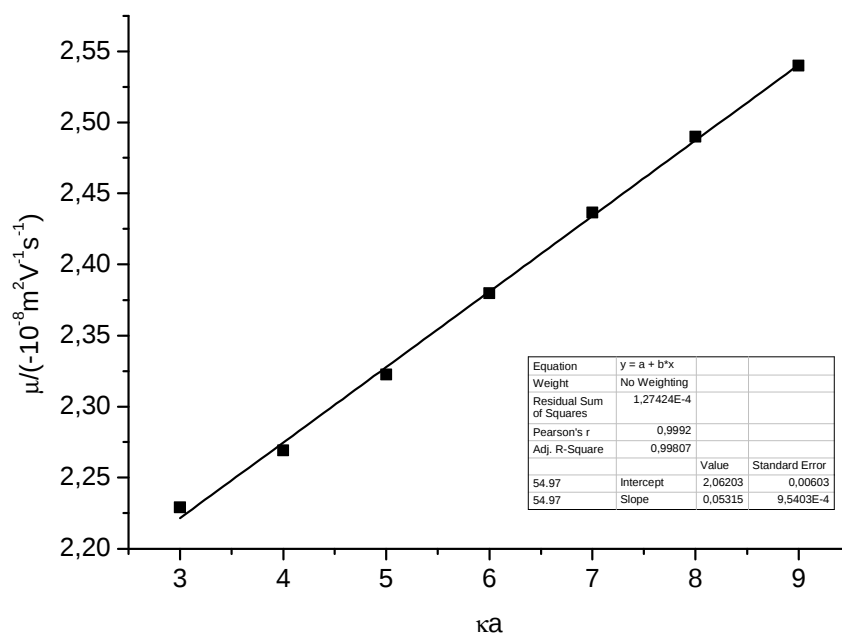


Figure S11b. Regression line for SNP12, T = 15 °C, c(borax) = 30 mmol L⁻¹.

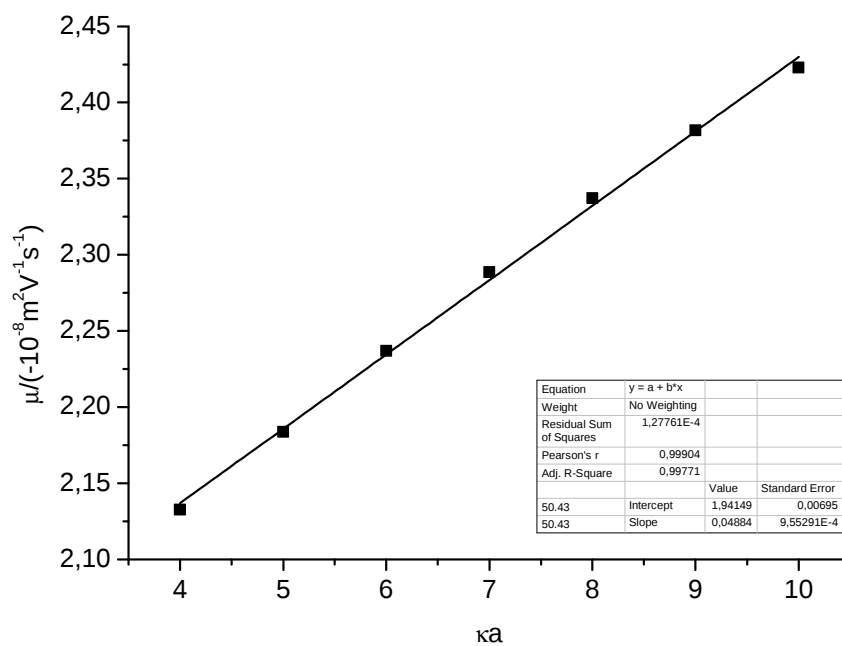


Figure S11c. Regression line for SNP12, T = 15 °C, c(borax) = 40 mmol L⁻¹.

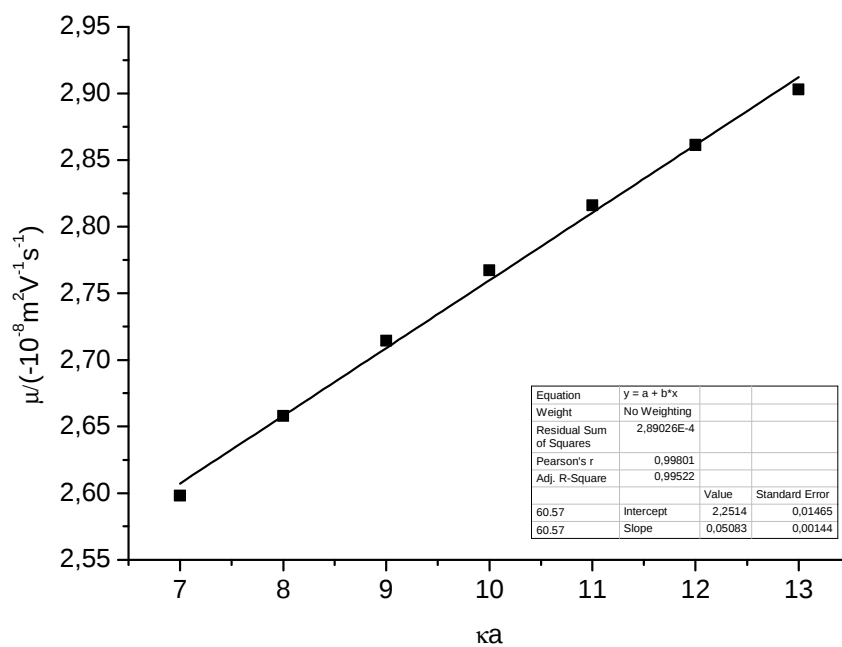


Figure S11d. Regression line for SNP22, T = 15 °C, c(borax) = 20 mmol L⁻¹.

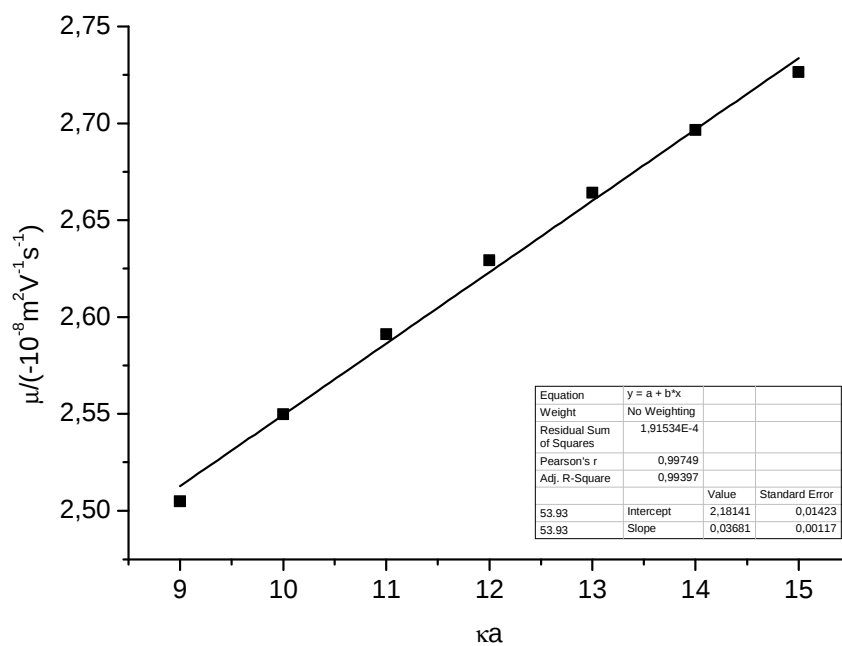


Figure S11e. Regression line for SNP22, T = 15 °C, c(borax) = 30 mmol L⁻¹.

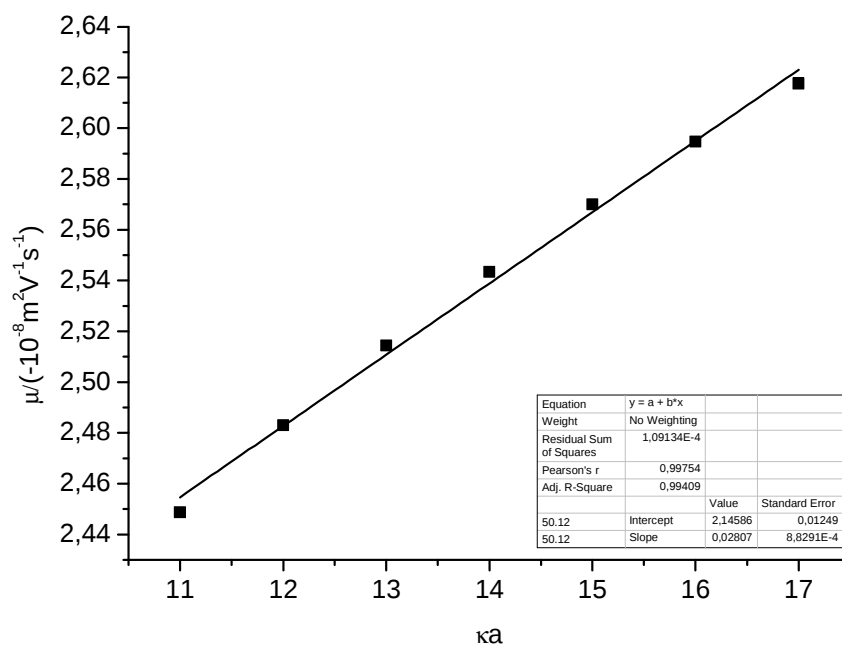


Figure S11f. Regression line for SNP22, T = 15 °C, c(borax) = 40 mmol L⁻¹.

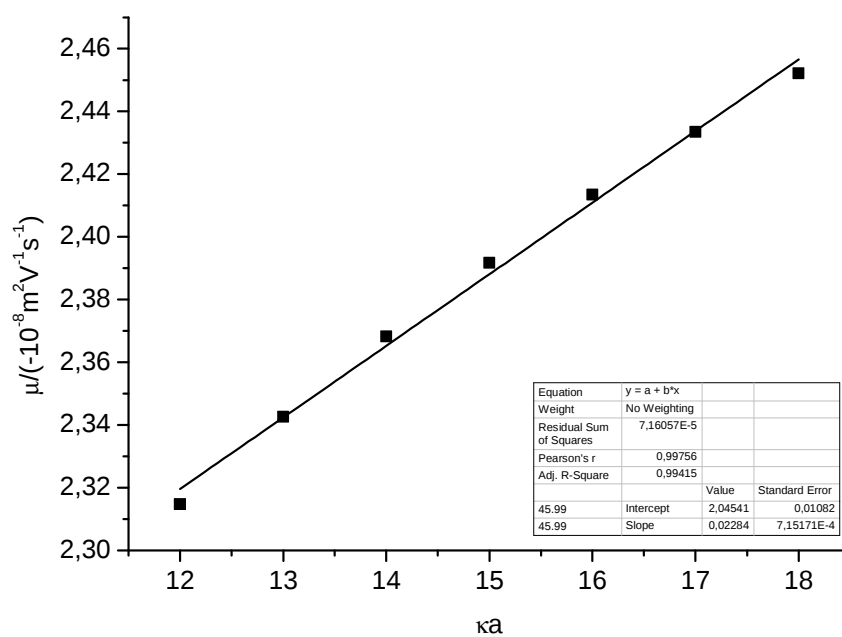


Figure S11g. Regression line for SNP22, T = 15 °C, c(borax) = 50 mmol L⁻¹.

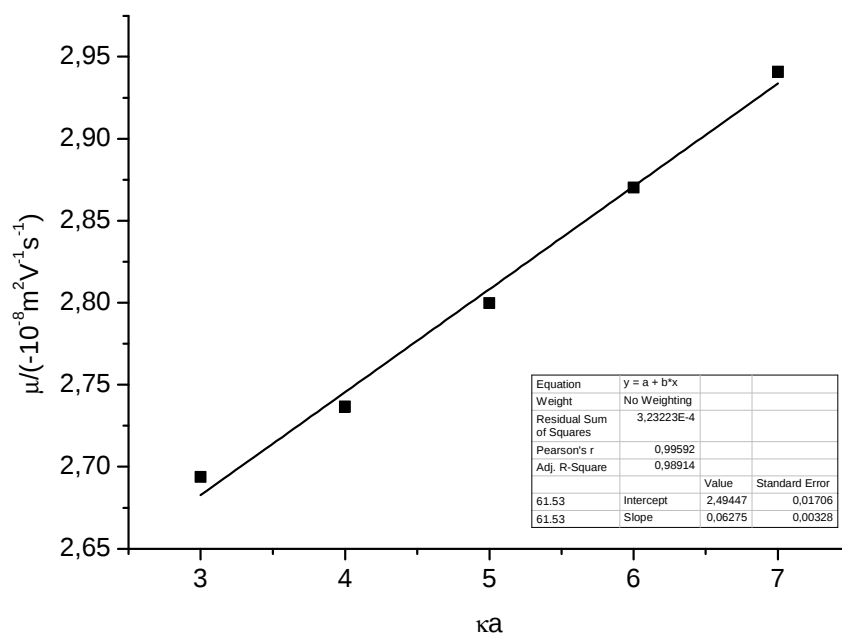


Figure S11h. Regression line for SNP12, T = 20 °C, c(borax) = 20 mmol L⁻¹.

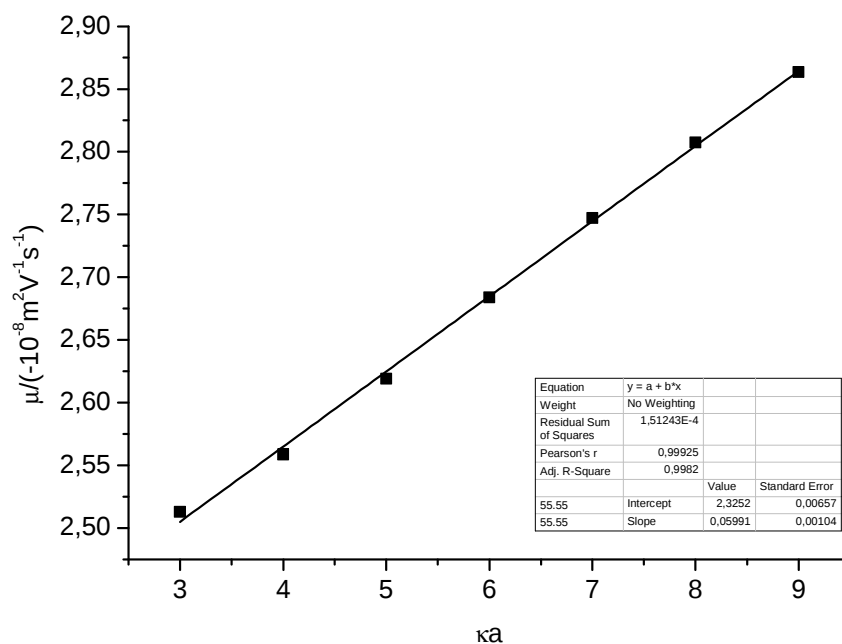


Figure S11i. Regression line for SNP12, T = 20 °C, c(borax) = 30 mmol L⁻¹.

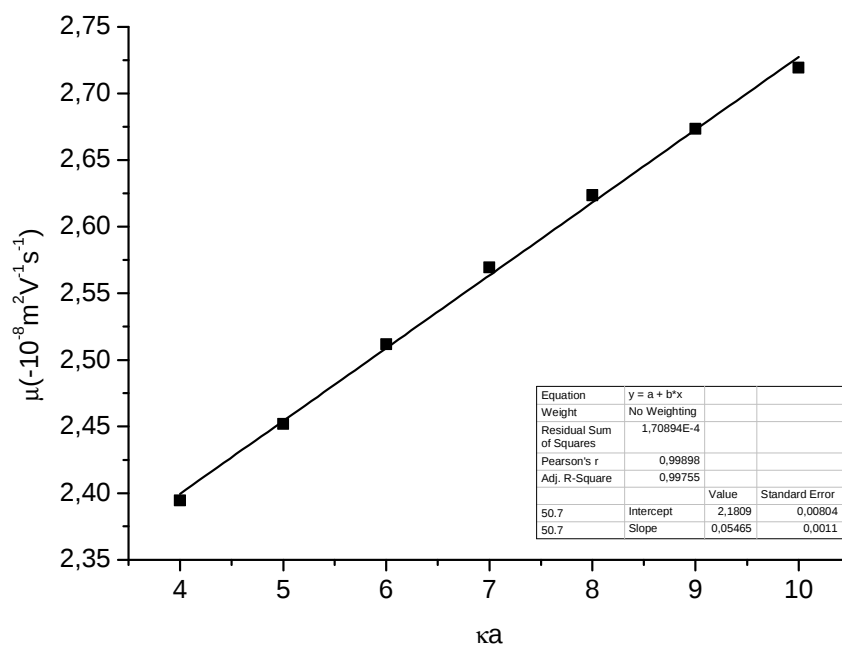


Figure S11j. Regression line for SNP12, T = 20 °C, c(borax) = 40 mmol L⁻¹.

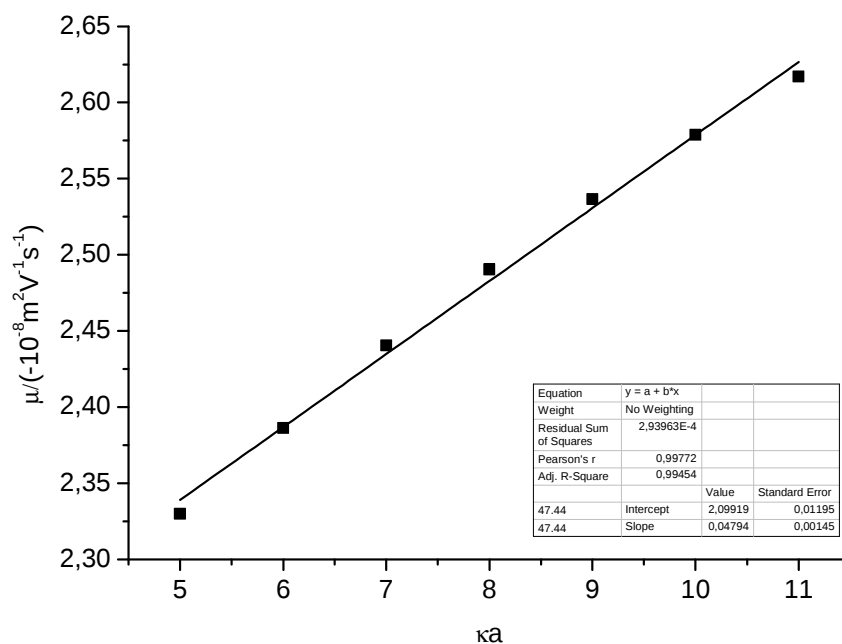


Figure S11k. Regression line for SNP12, T = 20 °C, c(borax) = 50 mmol L⁻¹.

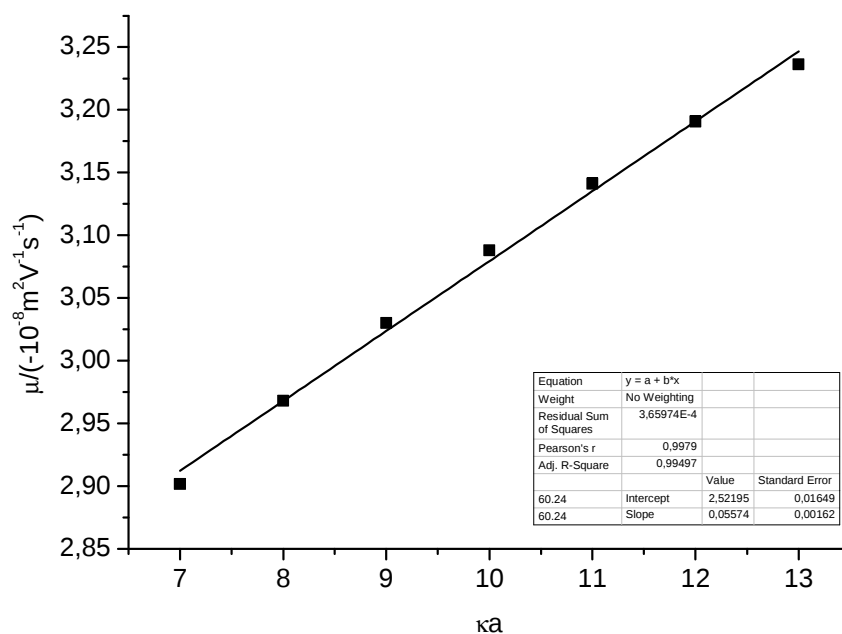


Figure S11l. Regression line for SNP22, T = 20 °C, c(borax) = 20 mmol L⁻¹.

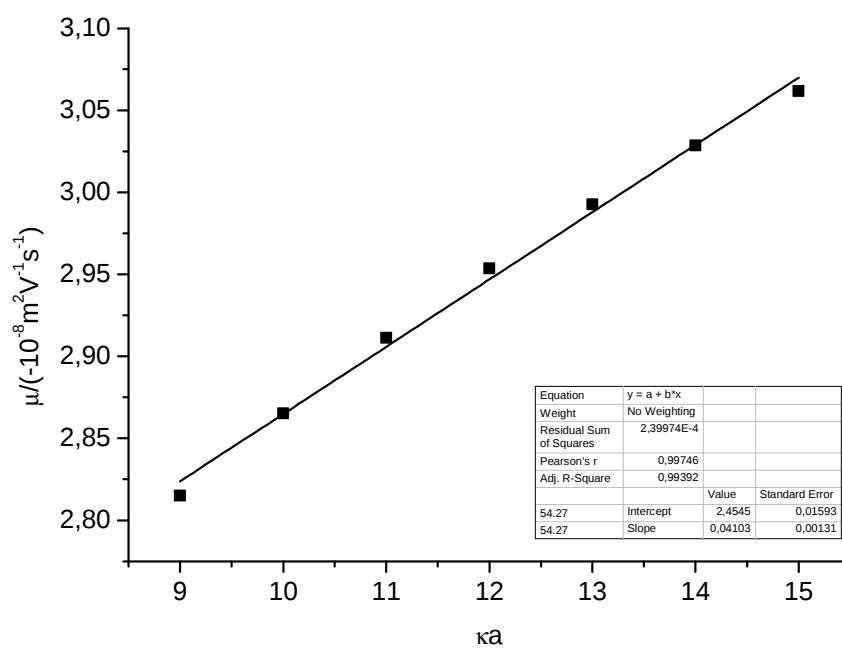


Figure S11m. Regression line for SNP22, T = 20 °C, c(borax) = 30 mmol L⁻¹.

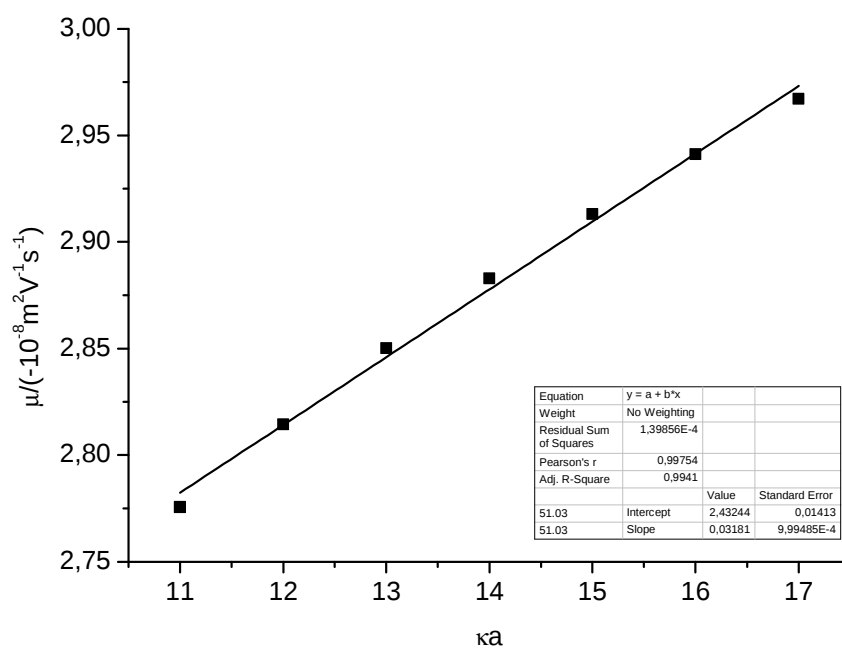


Figure S11n. Regression line for SNP22, T = 20 °C, c(borax) = 40 mmol L⁻¹.

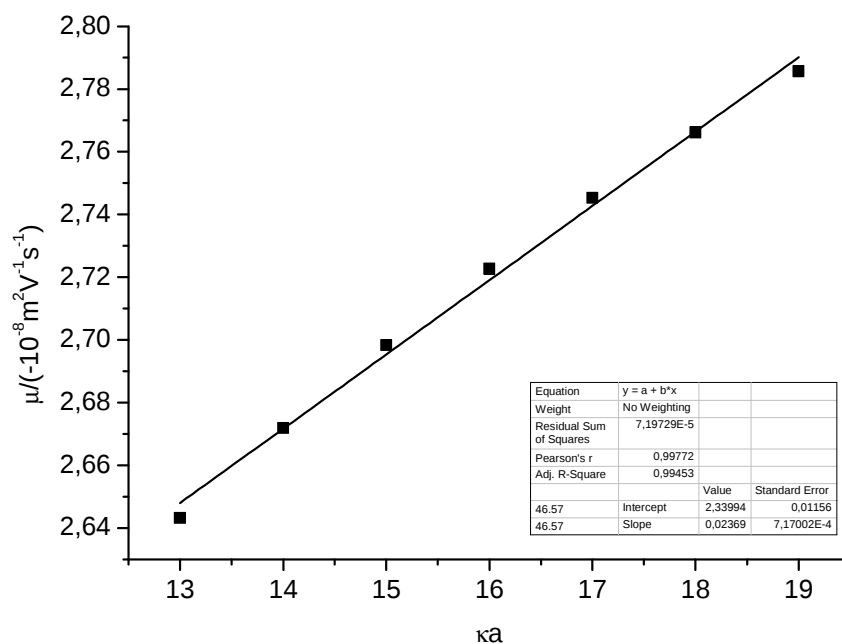


Figure S11o. Regression line for SNP22, T = 20 °C, c(borax) = 50 mmol L⁻¹.

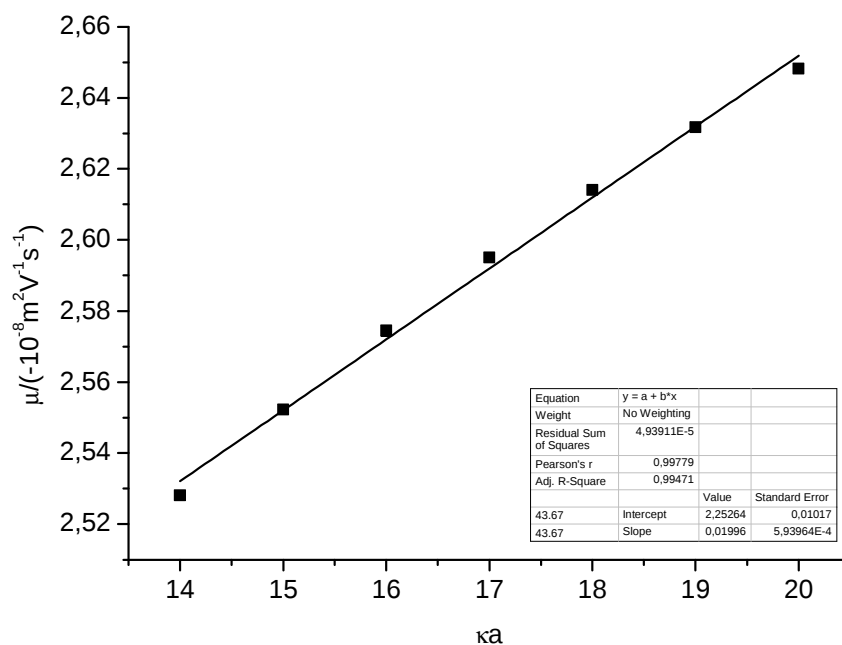


Figure S11p. Regression line for SNP22, T = 20 °C, c(borax) = 60 mmol L⁻¹.

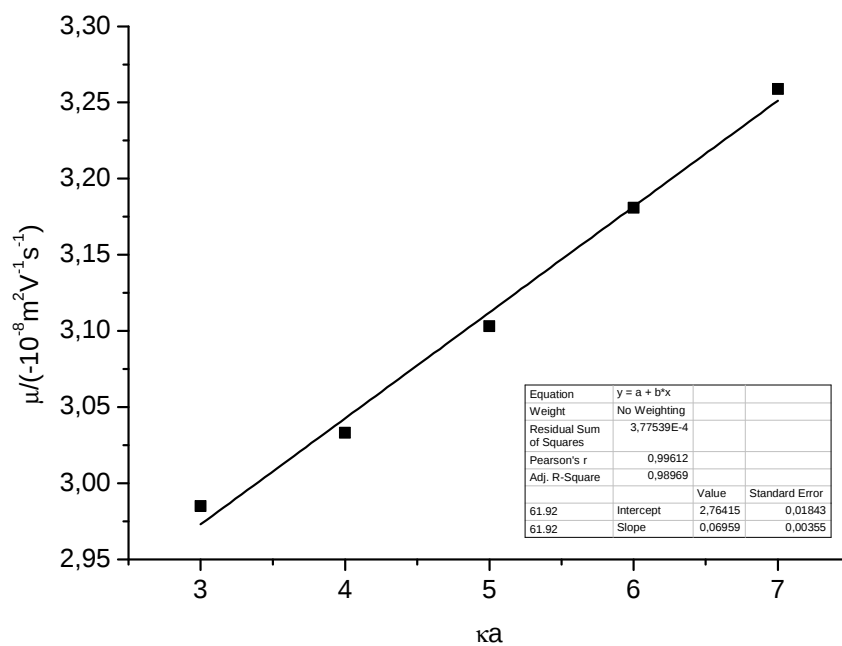


Figure S11q. Regression line for SNP12, T = 25 °C, c(borax) = 20 mmol L⁻¹.

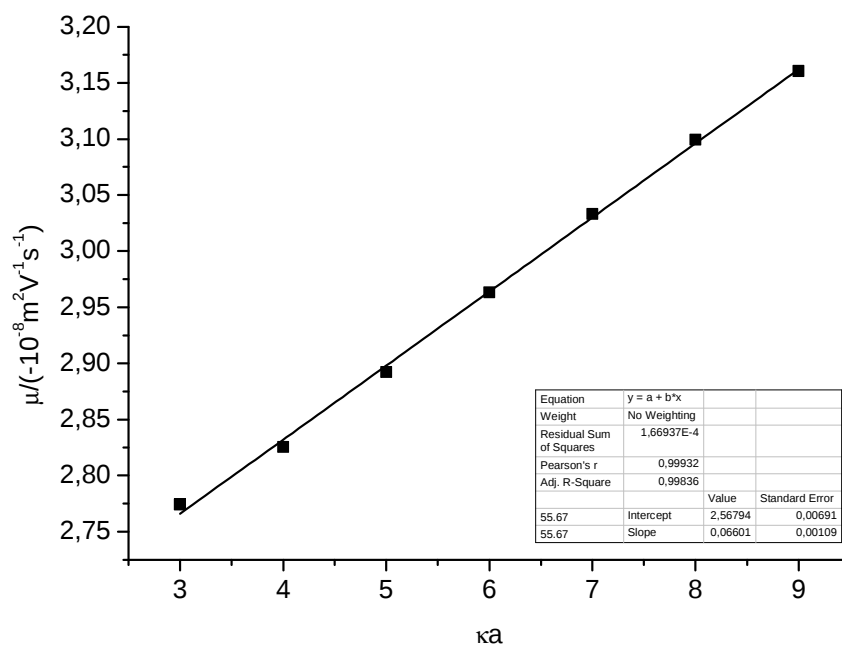


Figure S11r. Regression line for SNP12, T = 25 °C, c(borax) = 30 mmol L⁻¹.

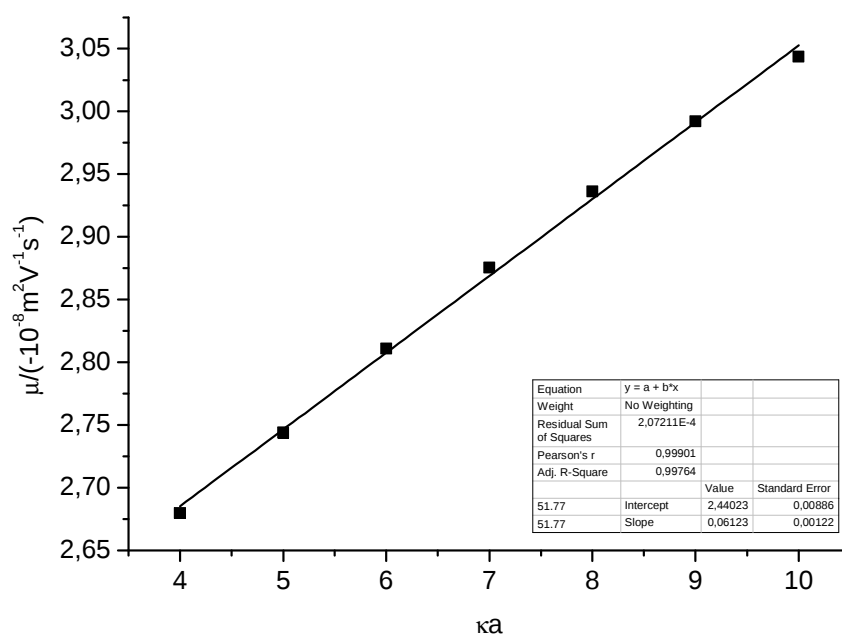


Figure S11s. Regression line for SNP12, T = 25 °C, c(borax) = 40 mmol L⁻¹.

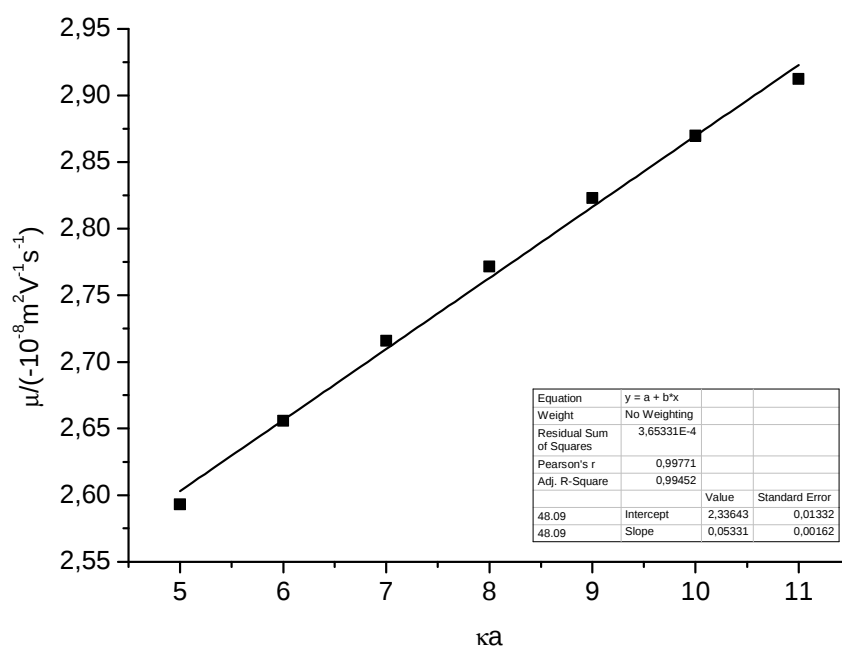


Figure S11t. Regression line for SNP12, T = 25 °C, c(borax) = 50 mmol L⁻¹.

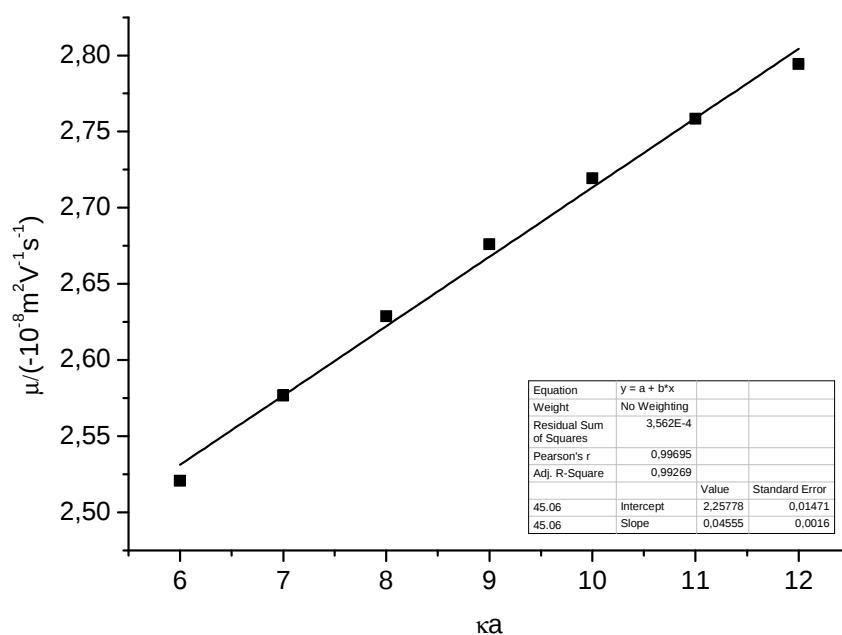


Figure S11u. Regression line for SNP12, T = 25 °C, c(borax) = 60 mmol L⁻¹.

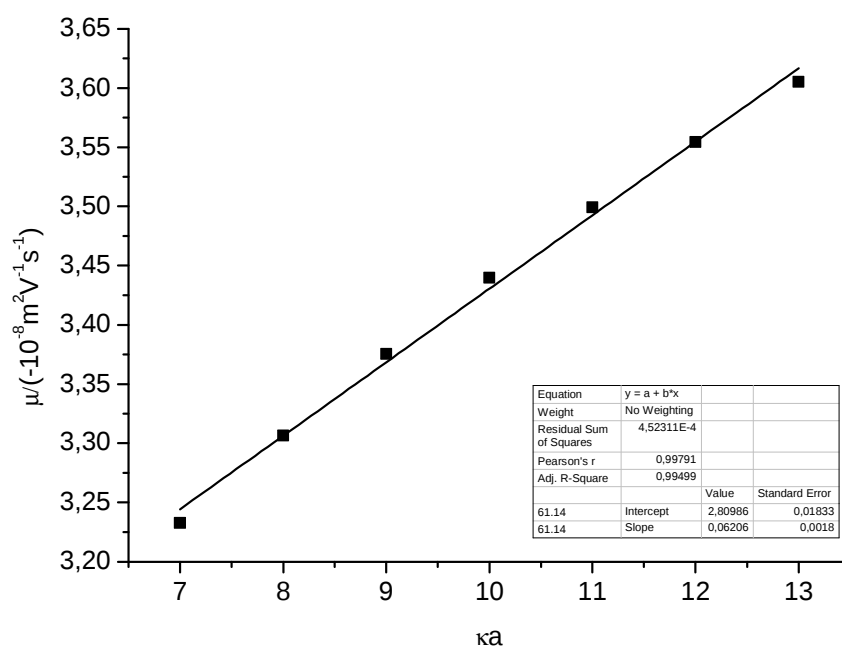


Figure S11v. Regression line for SNP22, T = 25 °C, c(borax) = 20 mmol L⁻¹.

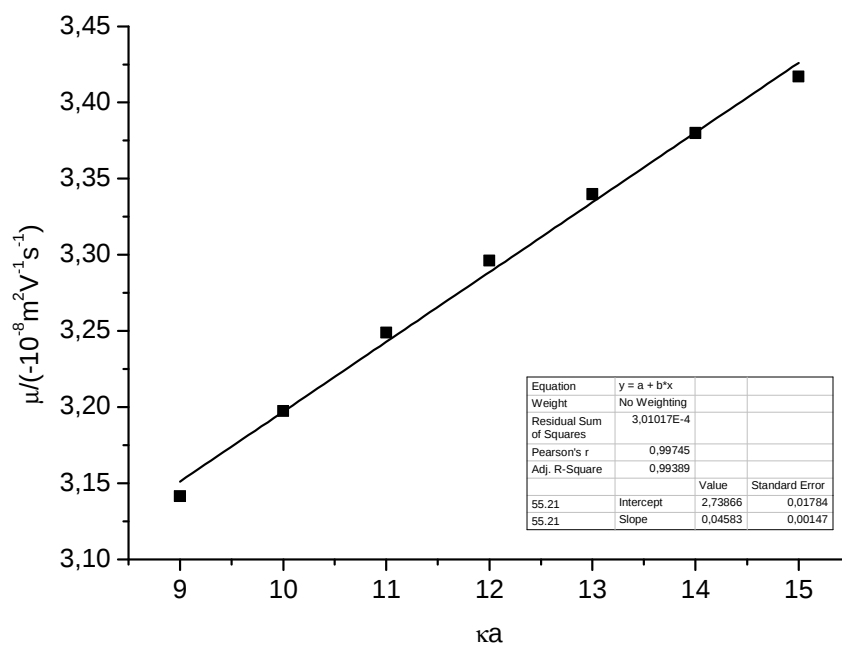


Figure S11w. Regression line for SNP22, T = 25 °C, c(borax) = 30 mmol L⁻¹.

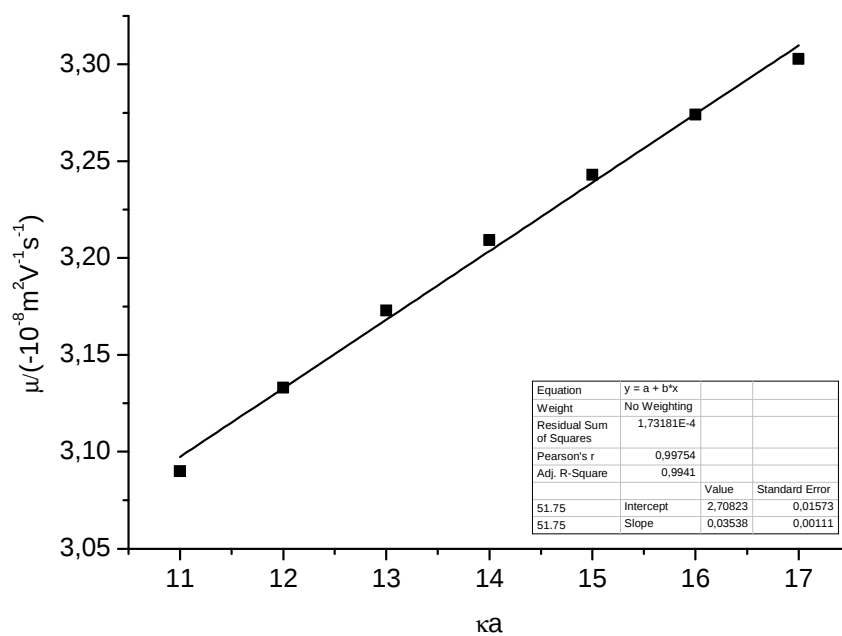


Figure S11x. Regression line for SNP22, T = 25 °C, c(borax) = 40 mmol L⁻¹.

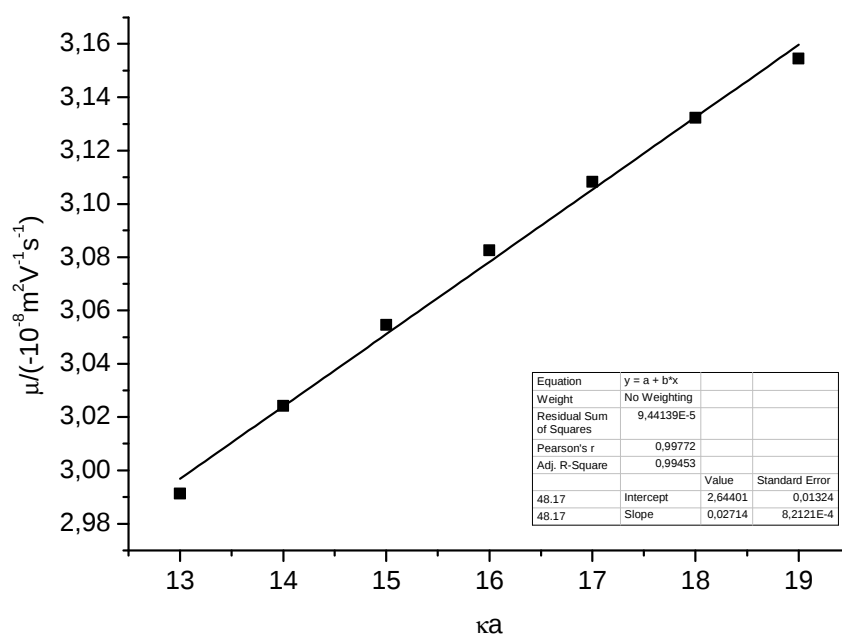


Figure S11y. Regression line for SNP22, T = 25 °C, c(borax) = 50 mmol L⁻¹.

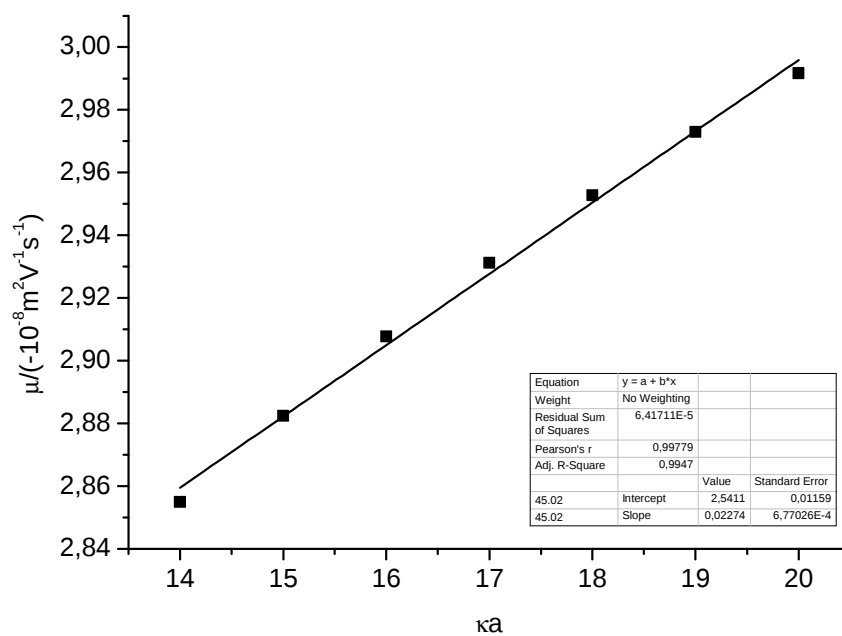


Figure S11z. Regression line for SNP22, T = 25 °C, c(borax) = 60 mmol L⁻¹.

Table S4. Overview on electrophoretic mobilities μ calculated from capillary electrophoresis data (mean values and standard deviation, N = 4, see also Tables S5a-g), for experimental parameters refer to Figure 3. The corresponding electropherograms are given in Figure S9.

Buffer concentration, temperature	SNP12 $\mu/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	SNP22 $\mu/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$
c(borax) = 20 mmol L ⁻¹ , T = 15 °C	-25.42 ($\pm$ 0.057)	-27.65 ($\pm$ 0.019)
c(borax) = 20 mmol L ⁻¹ , T = 20 °C	-28.28 ($\pm$ 0.078)	-30.88 ($\pm$ 0.014)
c(borax) = 20 mmol L ⁻¹ , T = 25 °C	-31.36 ($\pm$ 0.009)	-34.42 ($\pm$ 0.041)
1 st series		
c(borax) = 30 mmol L ⁻¹ , T = 15 °C	-24.14 ($\pm$ 0.035)	-26.36 ($\pm$ 0.026)
c(borax) = 30 mmol L ⁻¹ , T = 20 °C	-27.19 ($\pm$ 0.066)	-29.63 ($\pm$ 0.030)
c(borax) = 30 mmol L ⁻¹ , T = 25 °C	-30.09 ($\pm$ 0.011)	-33.09 ($\pm$ 0.067)
2 nd series		
c(borax) = 30 mmol L ⁻¹ , T = 15 °C	-24.23 ($\pm$ 0.040)	-26.31 ($\pm$ 0.071)
c(borax) = 30 mmol L ⁻¹ , T = 20 °C	-26.91 ($\pm$ 0.052)	-29.25 ($\pm$ 0.044)
c(borax) = 30 mmol L ⁻¹ , T = 25 °C	-29.88 ($\pm$ 0.060)	-33.31 ($\pm$ 0.185)
1 st series		
c(borax) = 40 mmol L ⁻¹ , T = 15 °C	-23.19 ($\pm$ 0.058)	-25.46
c(borax) = 40 mmol L ⁻¹ , T = 20 °C	-26.05 ($\pm$ 0.106)	-28.87 ($\pm$ 0.058)
c(borax) = 40 mmol L ⁻¹ , T = 25 °C	-29.25 ($\pm$ 0.041)	-32.07 ($\pm$ 0.034)
2 nd series		
c(borax) = 40 mmol L ⁻¹ , T = 15 °C	-23.20 ($\pm$ 0.047)	-25.23 ($\pm$ 0.022)
c(borax) = 40 mmol L ⁻¹ , T = 20 °C	-25.97 ($\pm$ 0.033)	-28.67 ($\pm$ 0.038)
c(borax) = 40 mmol L ⁻¹ , T = 25 °C	-29.17 ($\pm$ 0.065)	-32.16 ($\pm$ 0.038)
c(borax) = 50 mmol L ⁻¹ , T = 15 °C	-22.29	-24.08 ($\pm$ 0.054)
c(borax) = 50 mmol L ⁻¹ , T = 20 °C	-25.16 ($\pm$ 0.119)	-27.18 ($\pm$ 0.016)
c(borax) = 50 mmol L ⁻¹ , T = 25 °C	-28.02 ($\pm$ 0.042)	-30.79 ($\pm$ 0.101)
c(borax) = 60 mmol L ⁻¹ , T = 20 °C	----- ^a	-26.01 ($\pm$ 0.032)
c(borax) = 60 mmol L ⁻¹ , T = 25 °C	-26.94 ($\pm$ 0.200)	-29.40 ($\pm$ 0.080)

^a not determined

Table S5a. Determined electrophoretic mobilities and ζ potentials ($I = 40 \text{ mmol L}^{-1}$), for experimental parameters refer to Figures 3 and S9.

NP	Run	$\mu_{eo}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\mu_{ep}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP12 15 °C	1	42.920	-25.362	
	2	42.887	-25.392	
	3	42.876	-25.427	
	4	42.842	-25.494	
	5 ⁽²⁾	42.887	-25.427	
MW			-25.419	-62.42
SD			0.0571	
RSD			0.22%	
SNP12 20 °C	1	48.334	-28.193	
	2	48.263	-28.255	
	3	48.235	-28.294	
	4	48.292	-28.380	
	5 ⁽²⁾	48.278	-28.308	
MW			-28.281	-61.53
SD			0.0781	
RSD			0.28%	
SNP12 25 °C	1	54.398	-31.369	
	2	54.273	-31.365	
	3	54.183	-31.349	
	4	54.077	-31.362	
	5 ⁽²⁾	54.237	-31.336	
MW			-31.361	-61.92
SD			0.00868	
RSD			0.03%	
SNP22 15 °C	1	43.304	-27.678	
	2	43.213	-27.638	
	3	43.123	-27.641	
	4	43.077	-27.641	
	5 ⁽²⁾	43.179	-27.640	
MW			-27.649	-60.57
SD			0.0193	
RSD			0.07%	
SNP22 20 °C	1	48.995	-30.895	
	2	48.894	-30.876	
	3	48.836	-30.863	
	4	48.778	-30.887	
	5 ⁽²⁾	48.879	-30.889	
MW			-30.880	-60.24
SD			0.0137	
RSD			0.04%	
SNP22 25 °C	1	54.452	-34.475	
	2	54.506	-34.436	
	3	54.452	-34.380	
	4	54.416	-34.402	
	5 ⁽²⁾	54.434	-34.384	
MW			-34.423	-61.14
SD			0.0414	
RSD			0.12%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms

Table S5b. Determined electrophoretic mobilities and ζ potentials ($I = 60 \text{ mmol L}^{-1}$), for experimental parameters refer to Figures 3 and S9.

NP	Run	$\mu_{eo}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\mu_{ep}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP12 15 °C	1	37.245	-24.096	
	2	37.211	-24.176	
	3	37.144	-24.129	
	4	37.102	-24.160	
	5 ⁽²⁾	37.169	-24.114	
	MW		-24.140	-54.97
	SD		0.0353	
	RSD		0.15%	
SNP12 20 °C	1	42.055	-27.185	
	2	42.023	-27.197	
	3	42.023	-27.237	
	4	42.001	-27.330	
	5 ⁽²⁾	42.012	-27.217	
	MW		-27.247	-55.55
	SD		0.0657	
	RSD		0.24%	
SNP12 25 °C	1	45.949	-30.102	
	2	45.961	-30.100	
	3	45.974	-30.082	
	4	45.949	-30.082	
	5 ⁽²⁾	45.961	-30.095	
	MW		-30.091	-55.67
	SD		0.0109	
	RSD		0.04%	
SNP22 15 °C	1	37.203	-26.331	
	2	37.161	-26.362	
	3	37.144	-26.370	
	4	37.077	-26.394	
	5 ⁽²⁾	37.153	-26.359	
	MW		-26.364	-53.93
	SD		0.0261	
	RSD		0.10%	
SNP22 20 °C	1	41.651	-29.648	
	2	41.588	-29.613	
	3	41.598	-29.605	
	4	41.640	-29.668	
	5 ⁽²⁾	41.619	-29.650	
	MW		-29.634	-54.27
	SD		0.0297	
	RSD		0.10%	
SNP22 25 °C	1	46.532	-33.168	
	2	46.336	-33.005	
	3	46.480	-33.099	
	4	46.467	-33.085	
	5 ⁽²⁾	46.467	-33.094	
	MW		-33.089	-55.21
	SD		0.0668	
	RSD		0.20%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms

Table S5c. Determined electrophoretic mobilities and ζ potentials ($I = 60 \text{ mmol L}^{-1}$), for experimental parameters refer to Figures 3 and S9. **Reproducibility study.**

NP	Run	$\mu_{eo}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\mu_{ep}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP12 15 °C	1	37.380	-24.189	
	2	37.423	-24.202	
	3	37.414	-24.265	
	4	37.397	-24.263	
	5 ⁽²⁾	37.397	-24.241	
	MW		-24.230	-55.27
	SD		0.0399	
	RSD		0.16%	
SNP12 20 °C	1	42.023	-26.963	
	2	41.959	-26.842	
	3	41.937	-26.888	
	4	41.927	-26.928	
	5 ⁽²⁾	41.959	-26.910	
	MW		-26.905	-54.59
	SD		0.0521	
	RSD		0.19%	
SNP12 25 °C	1	46.797	-29.954	
	2	46.717	-29.830	
	3	46.717	-29.899	
	4	46.691	-29.831	
	5 ⁽²⁾	46.744	-29.913	
	MW		-29.878	-55.31
	SD		0.0599	
	RSD		0.20%	
SNP22 15 °C	1	37.144	-26.249	
	2	37.111	-26.302	
	3	37.094	-26.282	
	4	37.052	-26.414	
	5 ⁽²⁾	37.111	-26.314	
	MW		-26.312	-53.79
	SD		0.0713	
	RSD		0.27%	
SNP22 20 °C	1	41.746	-29.271	
	2	41.693	-29.210	
	3	41.683	-29.210	
	4	41.725	-29.298	
	5 ⁽²⁾	41.714	-29.254	
	MW		-29.247	-53.36
	SD		0.0440	
	RSD		0.15%	
SNP22 25 °C	1	46.467	-33.102	
	2	46.730	-33.399	
	3	46.823	-33.443	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	46.704	-33.064	
	MW		-33.315	-55.23
	SD		0.185	
	RSD		0.55%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms, ⁽³⁾ not determined

Table S5d. Determined electrophoretic mobilities and ζ potentials ($I = 80 \text{ mmol L}^{-1}$), for experimental parameters refer to Figures 3 and S9.

NP	Run	$\mu_{eo}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\mu_{ep}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP12 15 °C	1	33.067	-23.220	
	2	32.941	-23.113	
	3	32.875	-23.185	
	4	32.869	-23.247	
	5 ⁽²⁾	32.895	-23.128	
	MW		-23.191	-50.43
	SD		0.0577	
	RSD		0.58%	
SNP12 20 °C	1	38.018	-26.109	
	2	37.931	-26.152	
	3	37.740	-26.026	
	4	37.593	-25.911	
	5 ⁽²⁾	37.852	-26.116	
	MW		-26.049	-50.70
	SD		0.106	
	RSD		0.41%	
SNP12 25 °C	1	43.293	-29.246	
	2	43.281	-29.211	
	3	43.304	-29.294	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	43.293	-29.211	
	MW		-29.250	-51.77
	SD		0.0415	
	RSD		0.03%	
SNP22 15 °C	1	34.072	-25.456	
	2	----- ⁽³⁾	----- ⁽³⁾	
	3	----- ⁽³⁾	----- ⁽³⁾	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	----- ⁽³⁾	----- ⁽³⁾	
	MW		-25.456	-50.12
	SD			
	RSD			
SNP22 20 °C	1	38.761	-28.918	
	2	38.679	-28.889	
	3	38.570	-28.806	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	38.597	-28.676	
	MW		-28.871	-51.03
	SD		0.0580	
	RSD		0.20%	
SNP22 25 °C	1	43.741	-32.082	
	2	43.579	-32.035	
	3	43.533	-32.050	
	4	43.487	-32.111	
	5 ⁽²⁾	43.293	-31.902	
	MW		-32.069	-51.57
	SD		0.0339	
	RSD		0.11%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms, ⁽³⁾ not determined

Table S5e. Determined electrophoretic mobilities and ζ potentials ($I = 80 \text{ mmol L}^{-1}$), for experimental parameters refer to Figures 3 and S9. **Reproducibility study.**

NP	Run	$\mu_{eo}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\mu_{ep}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP12 15 °C	1	33.254	-23.189	
	2	33.153	-23.177	
	3	33.127	-23.161	
	4	33.127	-23.268	
	5 ⁽²⁾	33.147	-23.162	
	MW		-23.200	-50.46
	SD		0.0475	
	RSD		0.20%	
SNP12 20 °C	1	38.036	-25.983	
	2	38.018	-25.935	
	3	37.975	-26.011	
	4	37.896	-25.957	
	5 ⁽²⁾	38.001	-25.964	
	MW		-25.971	-50.50
	SD		0.033	
	RSD		0.13%	
SNP12 25 °C	1	42.887	-29.097	
	2	42.865	-29.163	
	3	42.809	-29.168	
	4	42.809	-29.256	
	5 ⁽²⁾	42.842	-29.167	
	MW		-29.171	-51.89
	SD		0.0653	
	RSD		0.22%	
SNP22 15 °C	1	33.682	-25.200	
	2	33.552	-25.241	
	3	33.511	-25.237	
	4	33.497	-25.248	
	5 ⁽²⁾	33.599	-25.277	
	MW		-25.232	-49.58
	SD		0.0217	
	RSD		0.08%	
SNP22 20 °C	1	38.815	-28.717	
	2	38.697	-28.639	
	3	38.606	-28.682	
	4	38.525	-28.637	
	5 ⁽²⁾	38.597	-28.676	
	MW		-28.669	-50.59
	SD		0.0382	
	RSD		0.13%	
SNP22 25 °C	1	43.338	-32.106	
	2	43.270	-32.182	
	3	43.270	-32.156	
	4	43.247	-32.189	
	5 ⁽²⁾	43.281	-32.176	
	MW		-32.159	-51.75
	SD		0.0377	
	RSD		0.12%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms

Table S5f. Determined electrophoretic mobilities and ζ potentials ($I = 100 \text{ mmol L}^{-1}$), for experimental parameters refer to Figures 3 and S9.

NP	Run	$\mu_{eo}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\mu_{ep}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP12 15 °C	1	30.576	-22.291	
	2	----- ⁽³⁾	----- ⁽³⁾	
	3	----- ⁽³⁾	----- ⁽³⁾	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	----- ⁽³⁾	----- ⁽³⁾	
	MW		-22.291	
	SD			
	RSD			
SNP12 20 °C	1	34.623	-25.032	
	2	34.623	-25.115	
	3	34.630	-25.193	
	4	34.674	-25.312	
	5 ⁽²⁾	34.630	-25.198	
	MW		-25.163	-47.44
	SD		0.119	
	RSD		0.47%	
SNP12 25 °C	1	38.870	-27.976	
	2	38.852	-28.075	
	3	38.834	-28.033	
	4	38.825	-28.006	
	5 ⁽²⁾	38.852	-28.032	
	MW		-28.022	-48.09
	SD		0.0419	
	RSD		0.15%	
SNP22 15 °C	1	----- ⁽³⁾	----- ⁽³⁾	
	2	30.689	-24.132	
	3	30.553	-24.025	
	4	30.525	-24.090	
	5 ⁽²⁾	30.587	-24.093	
	MW		-24.082	-45.99
	SD		0.0539	
	RSD		0.22%	
SNP22 20 °C	1	34.718	-27.163	
	2	34.660	-27.181	
	3	34.630	-27.170	
	4	34.645	-27.200	
	5 ⁽²⁾	34.652	-27.174	
	MW		-27.178	-46.57
	SD		0.0161	
	RSD		0.06%	
SNP22 25 °C	1	38.624	-30.917	
	2	38.552	-30.833	
	3	38.489	-30.701	
	4	38.534	-30.722	
	5 ⁽²⁾	38.561	-30.803	
	MW		-30.793	-48.07
	SD		0.101	
	RSD		0.33%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms, ⁽³⁾ not determined

Table S5g. Determined electrophoretic mobilities and ζ potentials ($I = 120 \text{ mmol L}^{-1}$), for experimental parameters refer to Figures 3 and S9.

NP	Run	$\mu_{eo}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\mu_{ep}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP12 15 °C	1	----- ⁽³⁾	----- ⁽³⁾	
	2	----- ⁽³⁾	----- ⁽³⁾	
	3	----- ⁽³⁾	----- ⁽³⁾	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	----- ⁽³⁾	----- ⁽³⁾	
MW				
SD				
RSD				
SNP12 20 °C	1	----- ⁽³⁾	----- ⁽³⁾	
	2	----- ⁽³⁾	----- ⁽³⁾	
	3	----- ⁽³⁾	----- ⁽³⁾	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	----- ⁽³⁾	----- ⁽³⁾	
MW				
SD				
RSD				
SNP12 25 °C	1	35.611	-26.783	
	2	35.580	-26.829	
	3	35.595	-26.924	
	4	35.588	-27.228	
	5 ⁽²⁾	35.595	-26.895	
MW			-26.941	-46.06
SD			0.200	
RSD			0.74%	
SNP22 15 °C	1	----- ⁽³⁾	----- ⁽³⁾	
	2	----- ⁽³⁾	----- ⁽³⁾	
	3	----- ⁽³⁾	----- ⁽³⁾	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	----- ⁽³⁾	----- ⁽³⁾	
MW				
SD				
RSD				
SNP22 20 °C	1	32.467	-26.014	
	2	32.391	-25.992	
	3	32.346	-25.983	
	4	32.416	-26.055	
	5 ⁽²⁾	32.384	-25.986	
MW			-26.011	-43.66
SD			0.0324	
RSD			0.12%	
SNP22 25 °C	1	35.758	-29.516	
	2	35.619	-29.363	
	3	35.673	-29.372	
	4	35.688	-29.340	
	5 ⁽²⁾	35.673	-29.380	
MW			-29.398	-45.02
SD			0.0800	
RSD			0.27%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms, ⁽³⁾ not determined

Table S5h. Determined electrophoretic mobilities and ζ potentials ($I = 80 \text{ mmol L}^{-1}$), for experimental parameters refer to Figures 3 and S10.

NP	Run	$\mu_{eo}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\mu_{ep}/(\text{mm}^2 \text{ kV}^{-1} \text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP7 15 °C 1 st ser.	1	33.307	-20.893	
	2	33.287	-20.612	
	3	33.207	-20.859	
	4	33.287	-20.935	
	5 ⁽²⁾	33.274	-20.982	
	MW		-20.825	-46.92
	SD		0.145	
	RSD		0.70%	
SNP7 20 °C 1 st ser.	1	38.203	-23.432	
	2	38.115	-23.436	
	3	38.045	-23.472	
	4	38.001	-23.408	
	5 ⁽²⁾	38.089	-23.436	
	MW		-23.437	-47.31
	SD		0.0266	
	RSD		0.11%	
SNP7 25 °C 1 st ser.	1	42.227	-26.260	
	2	42.369	-26.329	
	3	42.401	-26.230	
	4	42.314	-26.222	
	5 ⁽²⁾	42.325	-26.259	
	MW		-26.260	-48.30
	SD		0.0489	
	RSD		0.19%	
SNP7 15 °C 2 nd ser.	1	33.538	-20.848	
	2	33.477	-20.877	
	3	33.483	-20.970	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	33.483	-20.885	
	MW		-20.899	-47.14
	SD		0.0637	
	RSD		0.30	
SNP7 20 °C 2 nd ser.	1	38.150	-23.512	
	2	38.089	-23.464	
	3	38.027	-23.553	
	4	38.071	-23.519	
	5 ⁽²⁾	38.080	-23.527	
	MW		-23.512	-47.50
	SD		0.0366	
	RSD		0.16%	
SNP7 25 °C 2 nd ser.	1	42.865	-26.278	
	2	42.820	-26.257	
	3	42.798	-26.179	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	42.842	-26.294	
	MW		-26.238	-48.34
	SD		0.0519	
	RSD		0.20%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms, ⁽³⁾ not determined

Table S5i. Determined electrophoretic mobilities and ζ potentials ($T = 25\text{ }^{\circ}\text{C}$), for experimental parameters refer to Figures 3 and S10.

NP	Run	$\mu_{\text{eo}}/(\text{mm}^2\text{ kV}^{-1}\text{ s}^{-1})$	$\mu_{\text{ep}}/(\text{mm}^2\text{ kV}^{-1}\text{ s}^{-1})$	$\zeta/\text{mV}^{(1)}$
SNP7 $I = 40$ mmol L^{-1}	1	53.393	-28.230	
	2	53.393	-28.360	
	3	53.290	-28.145	
	4	53.203	-28.515	
	5 ⁽²⁾	53.341	-28.391	
	MW		-28.312	-56.19
	SD		0.161	
	RSD		0.60%	
SNP7 $I = 60$ mmol L^{-1}	1	47,294	-27.468	
	2	47.226	-27.538	
	3	47.375	-27.352	
	4	47.267	-27.383	
	5	47.158	-27.345	
	6	47.024	-27.434	
	7 ⁽²⁾	47.253	-27.377	
	MW		-27.417	-52.34
	SD		0.0833	
	RSD		0.30%	
SNP7 $I = 80$ mmol L^{-1} 1 st ser.	1	42.227	-26.260	
	2	42.369	-26.329	
	3	42.401	-26.230	
	4	42.314	-26.222	
	5 ⁽²⁾	42.325	-26.259	
	MW		-26.260	-48.30
	SD		0.0489	
	RSD		0.19%	
SNP7 $I = 80$ mmol L^{-1} 2 nd ser.	1	42.865	-26.278	
	2	42.820	-26.257	
	3	42.798	-26.179	
	4	----- ⁽³⁾	----- ⁽³⁾	
	5 ⁽²⁾	42.842	-26.294	
	MW		-26.238	-48.34
	SD		0.0519	
	RSD		0.20%	
SNP7 $I = 80$ mmol L^{-1} 3 rd ser.	1	42.876	-26.481	
	2	42.764	-26.353	
	3	42.709	-26.346	
	4	42.643	-26.425	
	5 ⁽²⁾	42.742	-26.352	
	MW		-26.401	-48.29
	SD		0.0638	
	RSD		0.24%	
SNP7 $I = 100$ mmol L^{-1}	1	38.652	-25.221	
	2	38.624	-25.265	
	3	38.579	-25.303	
	4	38.561	-25.335	
	5 ⁽²⁾	38.606	-25.298	
	MW		-25.281	-45.24
	SD		0.0493	
	RSD		0.20%	

⁽¹⁾ modified Ohshima approximation, ⁽²⁾ from superimposed electropherograms, ⁽³⁾ not determined

Table S6. Illustration of the iterative scheme employed for the determination of ζ via the modified analytic approximation (see Equation (2))

c(borax)/ (mmol L ⁻¹)	κa	$\mu_{\text{measured}}/$ (10 ⁻⁸ m ² s ⁻¹ V ⁻¹)	$\mu_{\text{calculated}}/$ (10 ⁻⁸ m ² s ⁻¹ V ⁻¹)	ζ/mV	T = 15 °C
40	5.31013	-2.08247	-2.0821	-46.91	SNP7
1 st series			-2.0824	-46.92	
			-2.0827	-46.93	
40	5.31013	-2.0899	-2.0897	-47.13	
2 nd series			-2.0900	-47.14	
			-2.0904	-47.15	
20	5.38725	-2.54185	-2.5416	-62.41	SNP12
			-2.5418	-62.42	
			-2.5421	-62.43	
30	6.59835	-2.4140	-2.4137	-54.96	
1 st series			-2.4140	-54.97	
			-2.4143	-54.98	
30	6.59835	-2.42295	-2.4228	-55.26	
2 nd series			-2.4231	-55.27	
			-2.4234	-55.28	
40	7.61888	-2.31912	-2.3186	-50.42	
1 st series			-2.3190	-50.43	
			-2.3193	-50.44	
40	7.61888	-2.31985	-2.3197	-50.45	SNP22
2 nd series			-2.3200	-50.46	
			-2.3204	-50.47	
20	9.95825	-2.76495	-2.7648	-60.56	
			-2.7651	-60.57	
			-2.7654	-60.58	
30	12.19695	-2.63643	-2.6359	-53.92	
1 st series			-2.6363	-53.93	
			-2.6367	-53.94	
30	12.19695	-2.63118	-2.6307	-53.78	
2 nd series			-2.6311	-53.79	
			-2.6314	-53.80	
40	14.08338	-2.5456	-2.5453	-50.11	SNP22
1 st series			-2.5457	-50.12	
			-2.5461	-50.13	
40	14.08338	-2.52315	-2.5229	-49.57	
2 nd series			-2.5233	-49.58	
			-2.5237	-49.59	
50	15.74928	-2.40821	-2.4076	-45.98	
			-2.4081	-45.99	
			-2.4085	-46.00	

c(borax)/ (mmol L ⁻¹)	κa	μ _{measured} / (10 ⁻⁸ m ² s ⁻¹ V ⁻¹)	μ _{calculated} / (10 ⁻⁸ m ² s ⁻¹ V ⁻¹)	ζ/mV	T = 20 °C
40 1 st series	5.33025	-2.3437	-2.3432 -2.3436 -2.3440	-47.30 -47.31 -47.32	SNP7
40 2 nd series	5.33025	-2.3512	-2.3506 -2.3510 -2.3514	-47.49 -47.50 -47.51	
20	5.40787	-2.82806	-2.8278 -2.8281 -2.8284	-61.52 -61.53 -61.54	
30 1 st series	6.62310	-2.72375	-2.7233 -2.7237 -2.7240	-55.54 -55.55 -55.56	SNP12
30 2 nd series	6.62310	-2.69050	-2.6900 -2.6904 -2.6907	-54.58 -54.59 -54.60	
40 1 st series	7.64775	-2.60492	-2.6046 -2.6050 -2.6054	-50.69 -50.70 -50.71	
40 2 nd series	7.64775	-2.59715	-2.5967 -2.5971 -2.5975	-50.49 -50.50 -50.51	
50	8.55030	-2.51629	-2.5159 -2.5163 -2.5167	-47.43 -47.44 -47.45	
20	9.99638	-3.08800	-3.0876 -3.0879 -3.0883	-60.23 -60.24 -60.25	
30 1 st series	12.2427	-2.96339	-2.9630 -2.9634 -2.9638	-54.26 -54.27 -54.28	
30 2 nd series	12.2427	-2.92474	-2.9243 -2.9248 -2.9252	-53.35 -53.36 -53.37	SNP22
40 1 st series	14.13675	-2.88712	-2.8867 -2.8872 -2.8876	-51.02 -51.03 -51.04	
40 2 nd series	14.13675	-2.86680	-2.8664 -2.8668 -2.8673	-50.58 -50.59 -50.60	
50	15.80510	-2.71785	-2.7176 -2.7181 -2.7186	-46.56 -46.57 -46.58	
60	17.31332	-2.60110	-2.6006 -2.6012 -2.6017	-43.65 -43.66 -43.67	

c(borax)/ (mmol L ⁻¹)	κa	$\mu_{\text{measured}}/(10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$	$\mu_{\text{calculated}}/(10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$	ζ/mV	T = 25 °C
20	3.78465	-2.8310	-2.8306	-56.18	SNP7
			-2.8310	-56.19	
			-2.8313	-56.20	
30	4.63507	-2.7420	-2.7416	-52.33	
			-2.7420	-52.34	
			-2.7424	-52.35	
40 1 st series	5.3521	-2.6240	-2.6238	-48.29	
			-2.6242	-48.30	
			-2.6246	-48.31	
40 2 nd series	5.3521	-2.6260	-2.6255	-48.33	
			-2.6259	-48.34	
			-2.6263	-48.35	
40 3 rd series	5.3521	-2.6238	-2.6233	-48.28	
			-2.6238	-48.29	
			-2.6242	-48.30	
50	5.98402	-2.5280	-2.5274	-45.23	
			-2.5279	-45.24	
			-2.5283	-45.25	
20	5.43015	-3.1360	-3.1358	-61.91	SNP12
			-3.1361	-61.92	
			-3.1364	-61.93	
30 1 st series	6.65033	-3.0090	-3.0088	-55.66	
			-3.0092	-55.67	
			-3.0096	-55.68	
30 2 nd series	6.65033	-2.9954	-2.9949	-55.30	
			-2.9953	-55.31	
			-2.9957	-55.32	
40 1 st series	7.6791	-2.9170	-2.9168	-51.76	
			-2.9172	-51.77	
			-2.9176	-51.78	
40 2 nd series	7.6791	-2.9250	-2.9219	-51.88	
			-2.9224	-51.89	
			-2.9228	-51.90	
50	8.58577	-2.8020	-2.8016	-48.08	
			-2.8021	-48.09	
			-2.8026	-48.10	
60	9.405	-2.6940	-2.6935	-45.05	
			-2.6940	-45.06	
			-2.6945	-45.07	

20	10.03755	-3.4420	-3.4418 -3.4422 -3.4426	-61.13 -61.14 -61.15	SNP22
30 1 st series	12.29303	-3.3090	-3.3088 -3.3093 -3.3098	-55.20 -55.21 -55.22	
30 2 nd series	12.29303	-3.31023	-3.3098 -3.3102 -3.3107	-55.22 -55.23 -55.24	
40 1 st series	14.1947	-3.2159	-3.2155 -3.2160 -3.2165	-51.74 -51.75 -51.76	
40 2 nd series	14.1947	-3.24082	-3.2403 -3.2408 -3.2413	-52.23 -52.24 -52.25	
40 3 rd series	14.1947	-3.2069	-3.2064 -3.2069 -3.2074	-51.56 -51.57 -51.58	
50	15.87068	-3.0793	-3.0784 -3.0790 -3.0795	-48.16 -48.17 -48.18	
60	17.385	-2.9397	-2.9391 -2.9397 -2.9403	-45.01 -45.02 -45.03	

Table S7. Calculated surface charge density σ_ζ at the shear plane for the interface fused silica/buffer at different temperatures (for experimental parameters refer to Figure S9).

c(borax)/ mmol L ⁻¹	κ/nm^{-1}	λ_D/nm	ζ/mV	$\sigma_\zeta/\text{C m}^{-2}$	capillary
T = 15 °C					
20	0.653	1.531	-67.22	-0.0430	
30	0.800	1.250	-58.12	-0.0425	
40	0.924	1.082	-51.98	-0.0421	
50	1.033	0.968	-47.78	-0.0421	
60	1.131	0.884	n. d.	n. d.	
MW				-0.0424	
SD				0.000451	
RSD				1.06%	
T = 20 °C					
20	0.655	1.527	-68.46	-0.0428	
30	0.803	1.245	-58.95	-0.0420	
40	0.927	1.079	-53.83	-0.0428	
50	1.036	0.965	-48.83	-0.0420	
60	1.135	0.881	-45.67	-0.0423	
MW				-0.0424	
SD				0.000385	
RSD				0.91%	
T = 25 °C					
20	0.658	1.520	-69.79	-0.0426	
30	0.806	1.241	-59.64	-0.0413	
40	0.931	1.074	-55.40	-0.0431	
50	1.041	0.961	-49.70	-0.0417	
60	1.140	0.877	-45.77	-0.0411	
MW				-0.0420	
SD				0000831	
RSD				1.98%	

MW: arithmetic mean; SD: standard deviation; RSD: relative standard deviation

Table S8. Calculated parameters of regression lines (for ranges of κa refer to Figures S11a-z)

T/°C	SNP ^a	ζ /mV	R	SSE/ (m ² V ⁻¹ s ⁻¹)	y-Interc./ (10 ⁻⁸ m ² V ⁻¹ s ⁻¹)	SE/ (10 ⁻⁸ m ² V ⁻¹ s ⁻¹)	Slope/ (10 ⁻⁸ m ² V ⁻¹ s ⁻¹)	SE/ (10 ⁻⁸ m ² V ⁻¹ s ⁻¹)
15	12(20)	-62.42	0.9948	3.29·10 ⁻⁴	2.246	0.0172	0.05613	0.00331
15	12(30)	-54.97	0.9981	1.27·10 ⁻⁴	2.062	0.00603	0.05315	0.000954
15	12(40)	-50.43	0.9990	1.28·10 ⁻⁴	1.941	0.00695	0.04884	0.000955
20	12(20)	-61.53	0.9959	3.23·10 ⁻⁴	2.494	0.0171	0.06275	0.00328
20	12(30)	-55.55	0.9993	1.51·10 ⁻⁴	2.325	0.00657	0.05991	0.00104
20	12(40)	-50.70	0.9990	1.71·10 ⁻⁴	2.181	0.00804	0.05465	0.00110
20	12(50)	-47.44	0.9977	2.94·10 ⁻⁴	2.099	0.0119	0.04794	0.00145
25	12(20)	-61.92	0.9962	3.77·10 ⁻⁴	2.764	0.0184	0.06959	0.00355
25	12(30)	-55.67	0.9993	1.67·10 ⁻⁴	2.568	0.00691	0.06601	0.00109
25	12(40)	-51.77	0.9990	2.07·10 ⁻⁴	2.440	0.00886	0.06123	0.00122
25	12(50)	-48.09	0.9977	3.65·10 ⁻⁴	2.336	0.0133	0.05331	0.00162
25	12(60)	-45.06	0.9970	3.56·10 ⁻⁴	2.258	0.0148	0.04555	0.00160
15	22(20)	-60.57	0.9980	2.89·10 ⁻⁴	2.251	0.0147	0.05083	0.00144
15	22(30)	-53.93	0.9975	1.92·10 ⁻⁴	2.181	0.0142	0.03681	0.00117
15	22(40)	-50.12	0.9975	1.09·10 ⁻⁴	2.146	0.0125	0.02807	0.000883
15	22(50)	-45.99	0.9976	7.16·10 ⁻⁵	2.045	0.0108	0.02284	0.000715
20	22(20)	-60.24	0.9979	3.66·10 ⁻⁴	2.522	0.0165	0.05574	0.00162
20	22(30)	-54.27	0.9975	2.39·10 ⁻⁴	2.455	0.0159	0.04103	0.00131
20	22(40)	-51.03	0.9975	1.40·10 ⁻⁴	2.432	0.0141	0.03181	0.000999
20	22(50)	-46.57	0.9977	7.20·10 ⁻⁵	2.340	0.0116	0.02369	0.000717
20	22(60)	-43.66	0.9978	4.94·10 ⁻⁵	2.253	0.0102	0.01996	0.000594
25	22(20)	-61.14	0.9979	4.52·10 ⁻⁴	2.810	0.0183	0.06206	0.00180
25	22(30)	-55.21	0.9975	3.01·10 ⁻⁴	2.739	0.0178	0.04583	0.00147
25	22(40)	-51.75	0.9975	1.73·10 ⁻⁴	2.708	0.0157	0.03538	0.00111
25	22(50)	-48.17	0.9977	9.44·10 ⁻⁵	2.644	0.0132	0.02714	0.000821
25	22(60)	-45.02	0.9978	6.42·10 ⁻⁵	2.541	0.0116	0.02274	0.000677

^a c(borax) in mmol L⁻¹ in brackets,

R = correlation coefficient, SSE = sum of squared errors, SE = standard error