

SUPPLEMENTARY INFORMATION TO THE PAPER

High-resolution ultrasonic spectroscopy study of interactions between hyaluronan and cationic surfactants

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Table ST 1. Molecular weights of hyaluronan products used in this work.

Product name	M_w^*	Batch number
kDa	kDa	
10-30	17	211-589
	16	211-263
	15	212-2069
90-130	116	210-493
	137	211-234
	101	212-1214
	116	212-2859
	117	213-3842
300-500	421	208-125
	430	212-2082
	458	213-3809
1500-1750	1730	210-636
	1800	211-180
	1697	212-1271
	1644	212-2298

* weight-average molecular weight provided by the supplier and obtained by SEC-MALS analysis.

Table ST 2. The critical micelle concentration, CMC, of the surfactants TTAB and CTAB in water and in sodium chloride solution at 25 °C measured by means of HR-US 102T, compared with the CMC from literature

Surfactant/environment	CMC mmol/l (this work)	CMC mmol/l
TTAB/water	3.7	3.7 ¹ , 3.7 ² , 3.5 ³ , 3.8 ⁴ , 3.7 ⁵ , 3.7 ⁶
CTAB/water	1.0	1.0 ¹ , 0.92 ² , 0.96 ³ , 0.92 ⁴ , 0.90 ⁵ , 0.92 ⁶ , 0.90 ⁷
TAB/0.15M NaCl	0.58	0.52 ⁸
CTAB/0.15M NaCl	0.070	0.062 ⁸

⁽¹⁾ Zieliński, R.; Ikeda, S.; Nomura, H.; Kato, S. *Journal of Colloid and Interface Science* **1989**, 129, 175-184.

⁽²⁾ Kudryashov, E.; Kapustina, T.; Morrissey, S.; Buckin, V.; Dawson, K.; Hirsch, E.; Candau, S. J.; Zana, R. *Journal of Colloid and Interface Science* **1998**, 203, 325-332.

⁽³⁾ Mosquera, V. *Journal of Colloid and Interface Science* **1998**, 206, 66-76.

⁽⁴⁾ González-Gaitano, G.; Crespo, A.; Tardajos, G. *The Journal of Physical Chemistry B* **2000**, 104, 1869-1879.

- (5) Buckin, V.; Kudryashov, E.; Morrissey, S.; Dawson, K.; Kapustina, T. *Trends in Colloid and Interface Science* **1998**, 110, 214-219.
- (6) Zieliński, R.; Ikeda, S.; Nomura, H.; Kato, S. *Journal of Colloid and Interface Science* 1987, 119, 398-408.
- (7) Buckin, V. *IOP Conference Series: Materials Science and Engineering* **2012**, 42.
- (8) Halasová, T.; Krouská, J.; Mravec, F.; Pekař, M. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2011**, 391, 25-31.

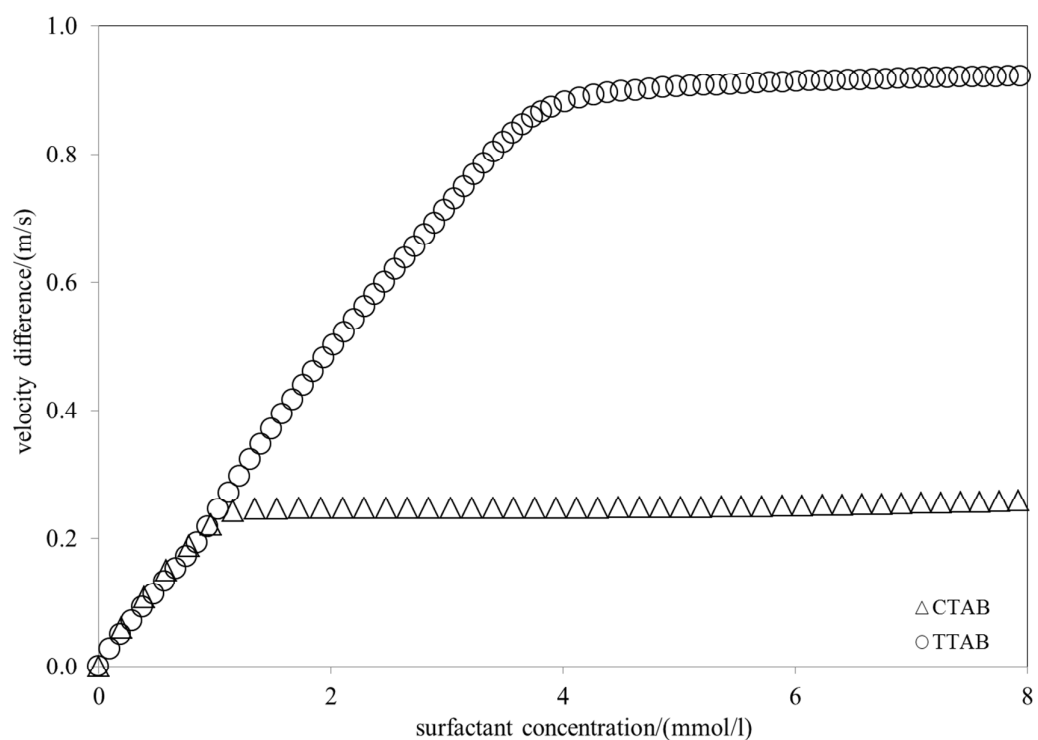


Figure SF1. Velocity titration profiles of surfactants in water.

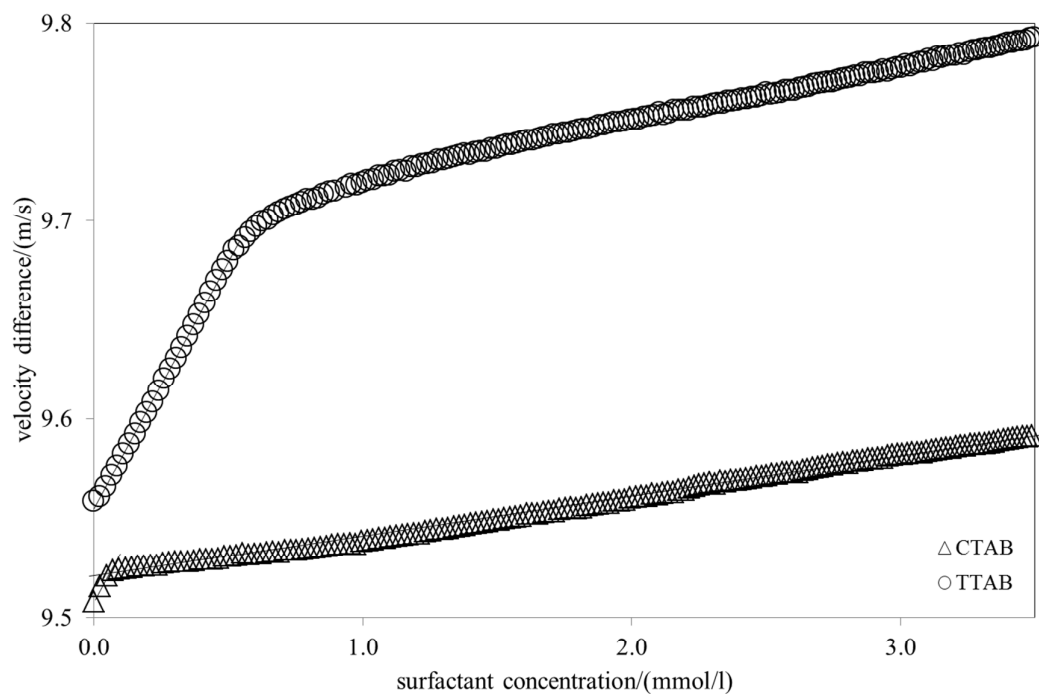


Figure SF2. Velocity titration profiles of surfactants in 0.15 M NaCl.

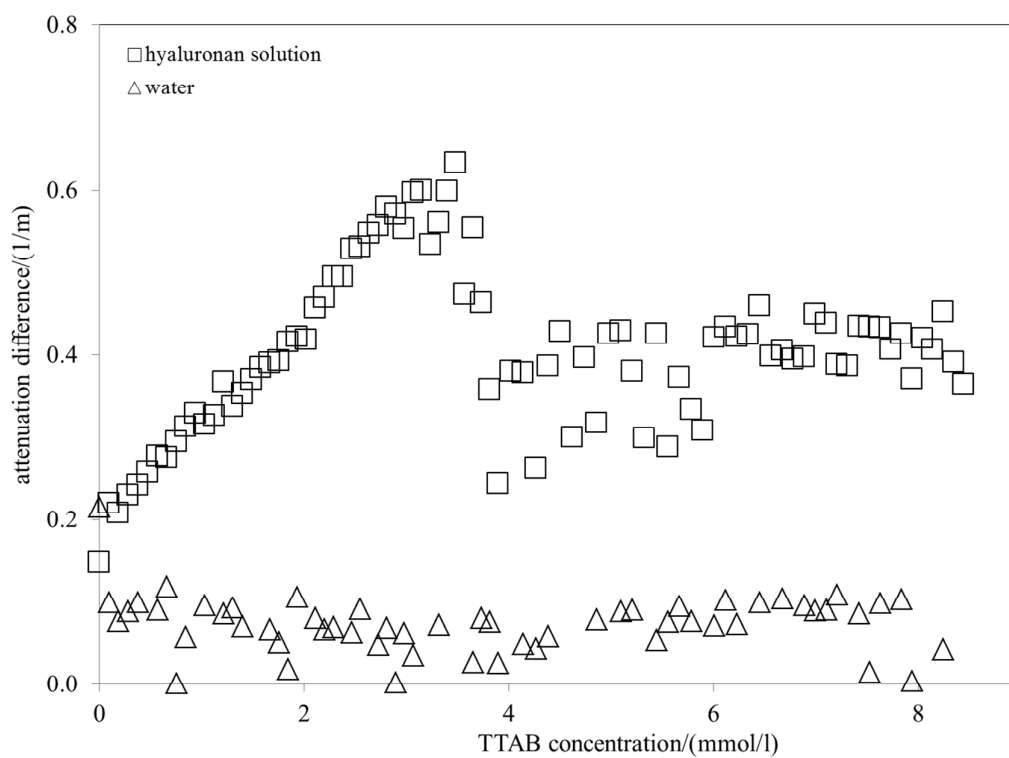


Figure SF3. The attenuation titration profiles for TTAB in water and in hyaluronan solution (300-500kDa, $w_0 = 1$ g/l; frequency 15 MHz; 25 °C). The curve for the titration in water was shifted to overlap the first points of both profiles.

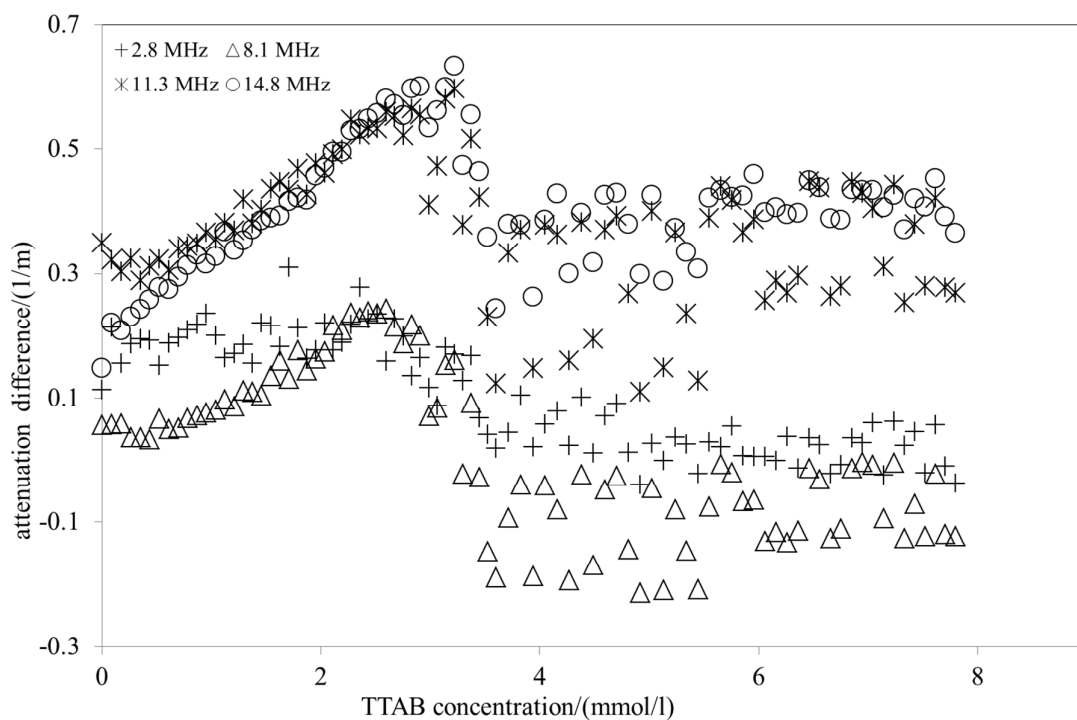


Figure SF4. The effect of frequency on the ultrasonic attenuation titration profile of the hyaluronan-TTABB system in water (hyaluronan 300-500 kDa, $w_0 = 1$ g/l, 25 °C).

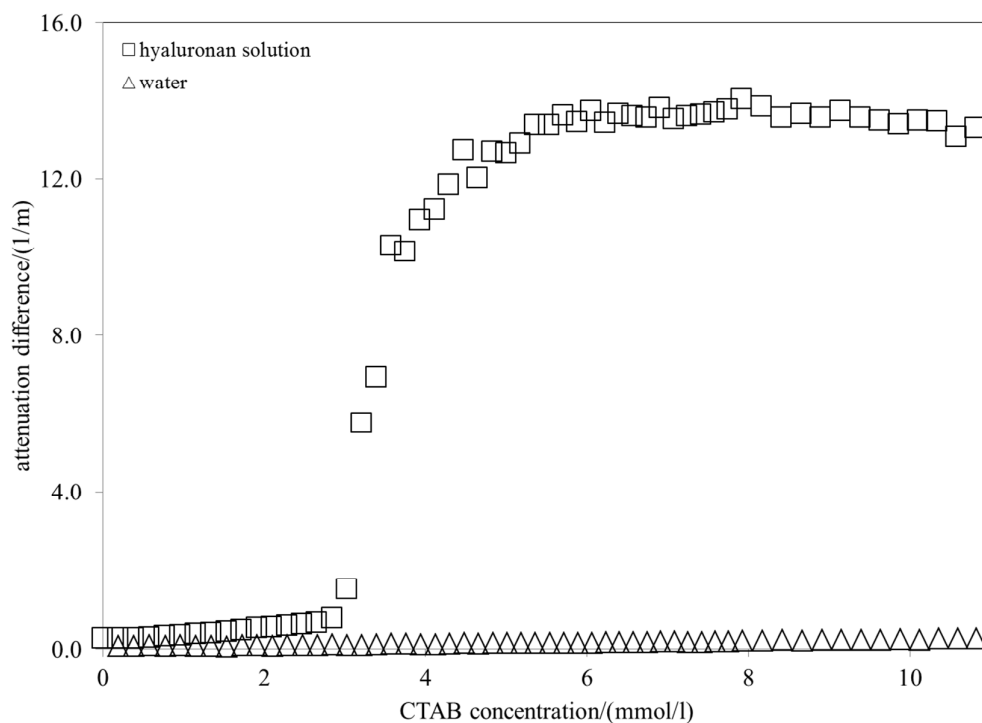


Figure SF5. The attenuation titration profiles for CTAB in water and in hyaluronan solution (300-500kDa, $w_0 = 1$ g/l; frequency 15 MHz; 25 °C). The curve for the titration in water was shifted to overlap the first points of both profiles.

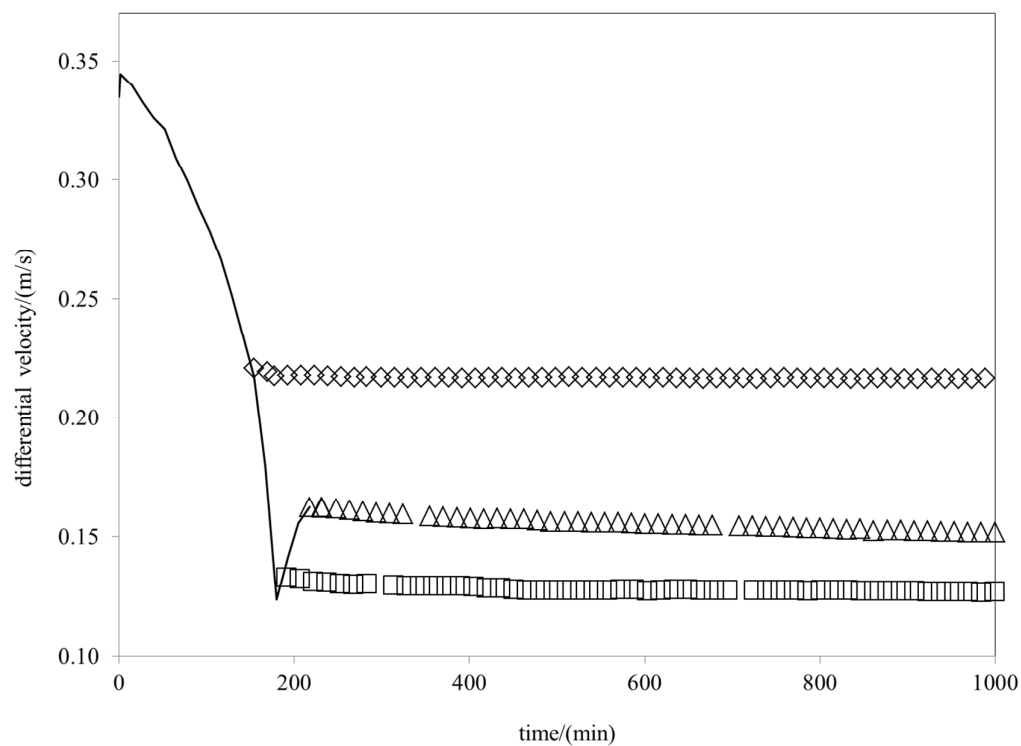


Figure SF6. Titration profiles of stopped-titrations with CTAB and hyaluronan solution in water (300-500 kDa, $w_0 = 1$ g/l); frequency 15 MHz, temperature 25°C. Solid line illustrates the original titration and points correspond to three stopped titrations in parts II-IV.

Titration profiles for CTAB in the hyaluronan-NaCl system (Figure SF7). Part I is missing and the behavior in parts II-IV is similar to TTAB (the change in slope within part IV is more marked). The velocity increases before the critical micellar concentration, but is higher than in the absence of hyaluronan; the slope of this increase is smaller beyond this concentration and a narrow interval of almost constant velocity appears at a much higher surfactant concentration than the critical micellar concentration. The CTAB concentration corresponding to this constant interval is very similar to that for TTAB; the charge ratio here is also around 1.3 (Table 2). The re-increase in the velocity after this interval is clearly (in contrast to TTAB) composed of at least two more or less linear branches intersecting around the CTAB concentration of 6 mmol/l. The initial increasing part corresponds visually to a clear system; during the constant interval some flakes or flocs and the evolution of turbidity can be observed. After this interval the system is cloudy.

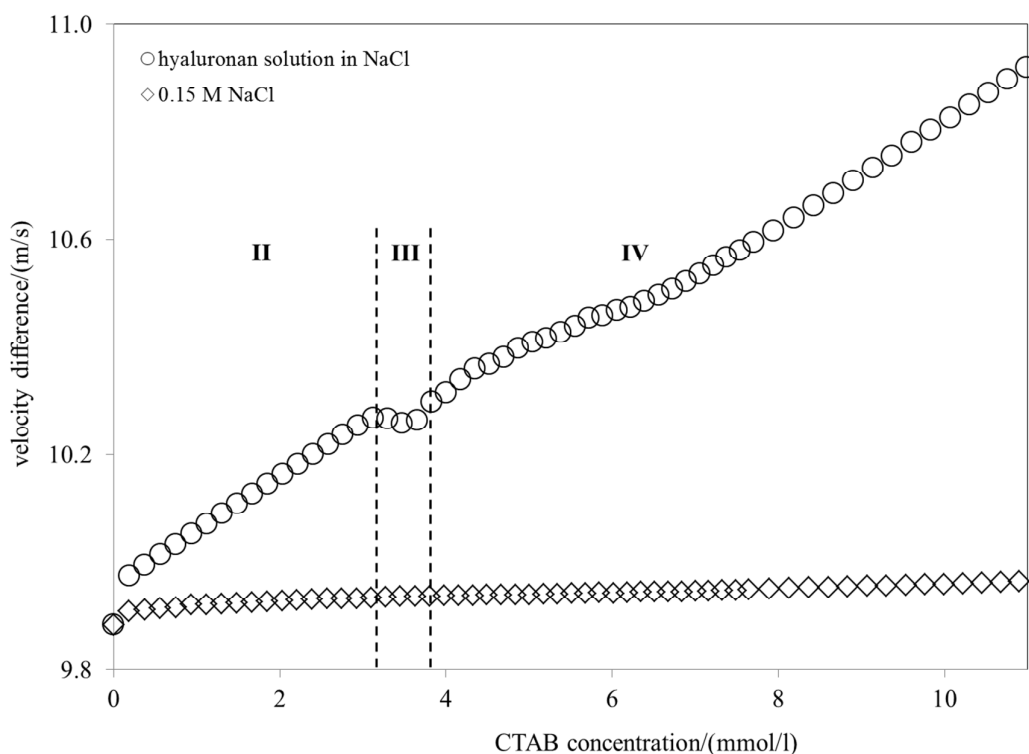


Figure SF7. The velocity titration profiles for CTAB in 0.15 M NaCl and in hyaluronan solution (300-500kDa, $w_0 = 1$ g/l; frequency 15 MHz; 25 °C). The curve for the titration in NaCl was shifted to overlap the first points of both profiles.

The attenuation reflects the changes in velocity (Figure SF8). Before the short region of constant velocity, the attenuation increases moderately, then sharply within this region, and even beyond it. Then it remains essentially constant up to the change mentioned in the

preceding paragraph, which appears around the CTAB concentration of 6 mmol/l, and above this concentration it increases again.

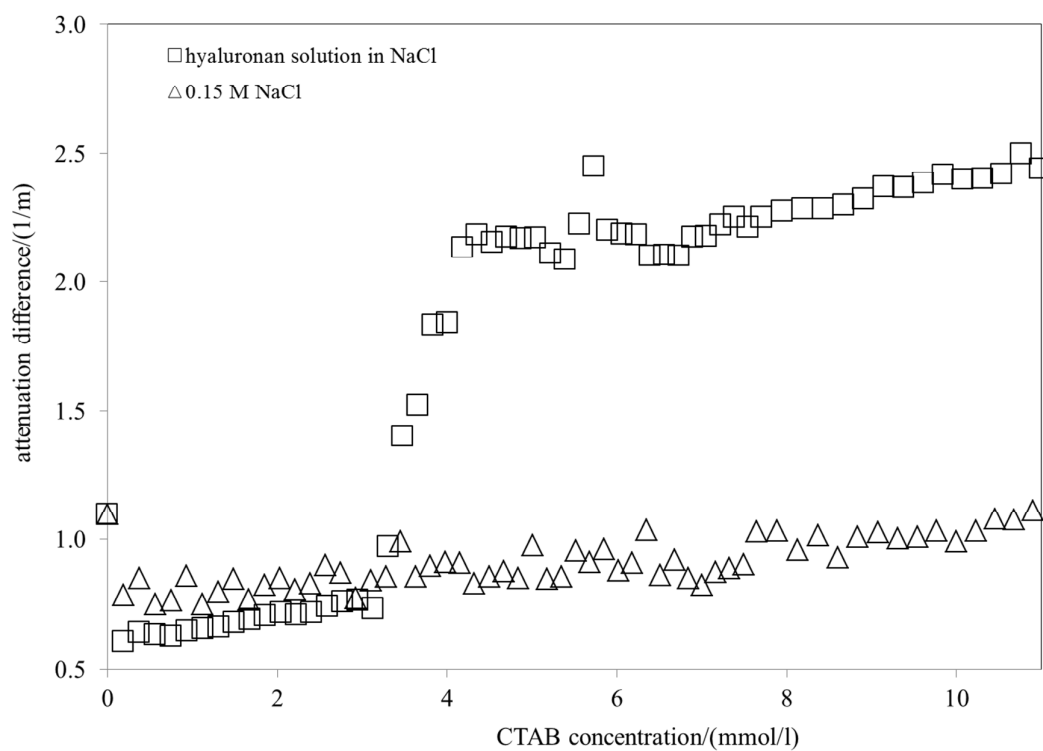


Figure SF8. The attenuation titration profiles for CTAB in 0.15 M NaCl and in hyaluronan solution (300-500kDa, $w_0 = 1$ g/l; frequency 15 MHz; 25 °C). The curve for the titration in NaCl was shifted to overlap the first points of both profiles.

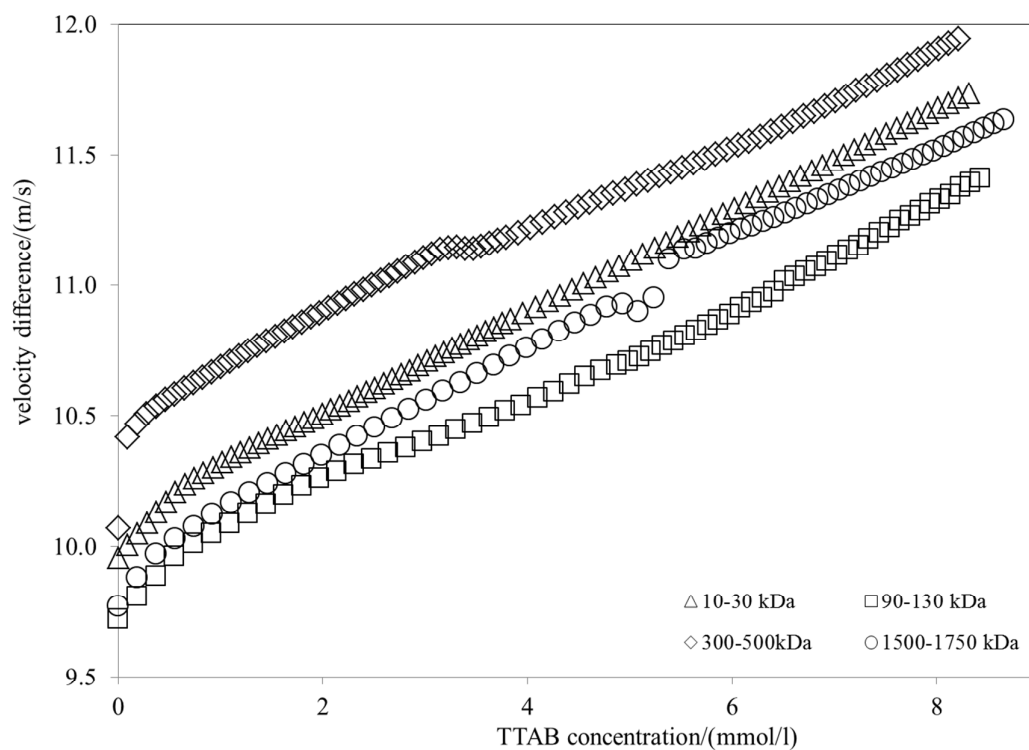


Figure SF9. Effect of hyaluronan molecular weight on the velocity titration profile in the hyaluronan-TTAB system in 0.15 M NaCl (25 °C, frequency 15 MHz; hyaluronan $w_0 = 1$ g/l).