Electronic Supplementary Information (ESI) for

Time-pH and Time-Humidity Scaling of Ionic Conductivity Spectra of Polyelectrolyte Multilayers

Jannis Schlicke, Cornelia Cramer and Monika Schönhoff

Institute of Physical Chemistry, University of Münster, Corrensstraße 28/30, 48149 Münster, Germany and Center for Soft Nanoscience, Busso-Peuss-Str. 10, 48149 Münster, Germany.

Relative Humidity via Saturated Salt Solutions

Table S1 shows the saturated salt solutions and the relative humidity values achieved as well as the literature values utilized during the Time-Humidity superposition studies.

Table S1: Relative humidity adjusted via saturated salt solutions. Both literature values as well as the experimental conditions are listed considering an error of 2 %, which is based on overall standard deviations.

Salt	Equilibrium relative humidity	Literature Value (25 °C)[1-3]
Lithium chloride	(8 ± 2) %	11.3 %[1, 3]
Potassium acetate	(22 ± 2) %	22.2 %[1, 3]
Magnesium chloride	(32 ± 2) %	32.7 %[1, 3]
Potassium Carbonate	(48 ± 2) %	43 %[3]
Magnesium nitrate	(54 ± 2) %	52.8 %[1]
Ammonium nitrate	(63 ± 2) %	63 %[2]
Sodium chloride	(79 ± 2) %	75 %[1, 3]
Potassium Sulfate	(99 ± 2) %	97.3 %[1, 3]

Time-RH Superposition

The evaluation of humidity-dependent conductivity spectra of (PDADMA/PAA)$_n$ PEMs reveals the applicability of superposition principle. Apart from samples prepared from water adjusted to pH 4 (Figure 2), samples prepared from 0.1 M LiCl solutions adjusted to pH 6 and 7.5 were investigated (Figure S1). According to previous findings[4] these samples are more likely to feature extrinsic charge compensation. Accordingly, significant deviations from Summerfield-type scaling are observed (Figure 5). This might indicate a varying charge carrier density.
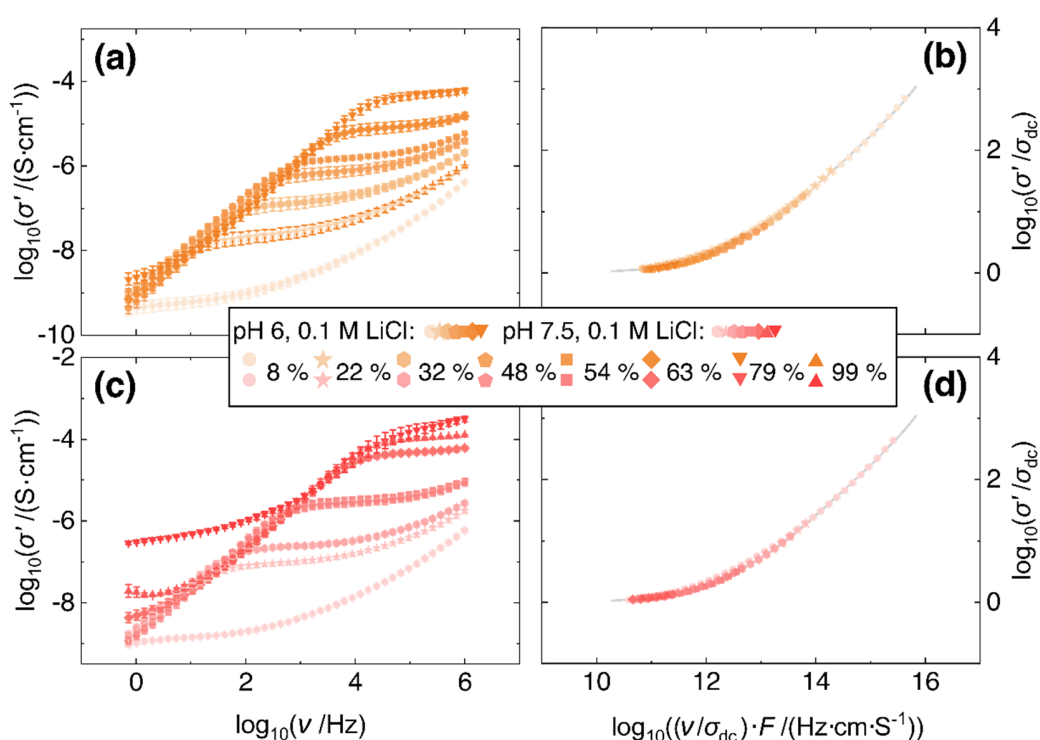

Figure S1: Time-humidity superposition of conductivity spectra of (PDADMA/PAA)$_n$ PEMs. Spectra obtained for different preparation pH and humidity are shifted with respect to the spectrum for samples prepared at pH 4 and measured at the lowest observed relative humidity. (a) and (b): Data for samples prepared from 0.1 M LiCl solutions at pH 6 measured at different relative humidity. (c) and (d): Data for samples prepared from 0.1 M LiCl solutions at pH 7.5 measured at different relative humidity.

References

1. Rockland, L. B., Anal. Chem., 1960, **32 (10)**, 1375-1376.

2. Young, J. F., *J. Appl. Chem*. 1967, **17 (9)**, 241-245.

3. Greenspan, L., J. *Res. Natl. Bur. Stand. A,* 1977, **81 (1)**, 89

4. Schlicke, J.; Hoffmann, K.; Lorenz, M.; Schönhoff, M.; Cramer, C., J. Phys. Chem. C, 2020, **124 (31)**, 16773-16783.