Automated Continuous Mixing (ACM) for equilibrium characterization techniques

The motivation behind automating equilibrium characterization techniques is to be able to analyze complex, multi-component systems, increase the resolution of experiments, allow for higher sample throughput, and, yes, to free students and co-workers from tedious tasks, like mixing many polymer solution samples.

Many types of characterizations are possible. Here, we mention three recent developments: Automated Zimm plot determination, the investigation of polyelectrolyte properties, and the association of charged micelles with neutral polymers:

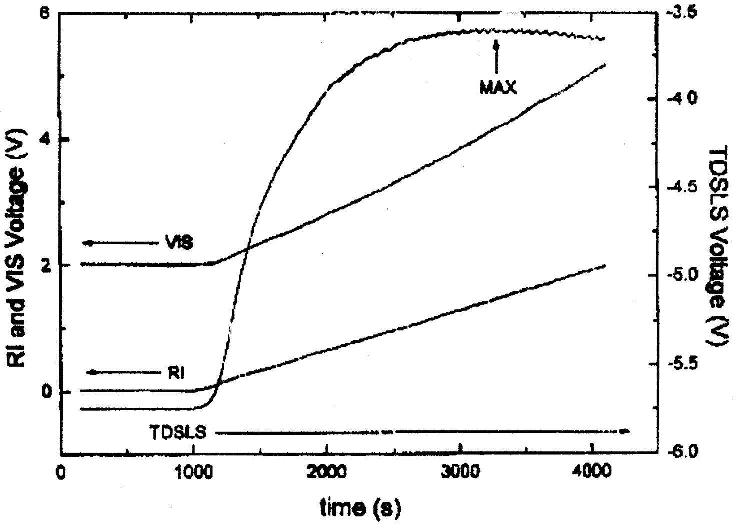
Automated determination of Zimm plots and intrinsic viscosity.

The binary mixing feature of a programmable mixer is used to automatically and continuously dilute a stock solution of polymer, poly(vinylpyrrolidone), or PVP, in this case. The same train of RI, light scattering (TDSLS), and viscosity detectors (without the UV detector in this case) are used as in SEC and online polymerization monitoring. (See Strelitzki and Reed, J. App. Polym. Sci., 73, 2359-2368, 1999)

Automated Polymer Solution Characterization

- Raw TDSLS, RI and Visc. data

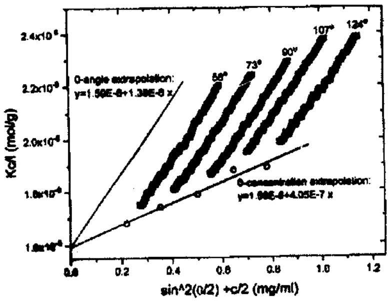
Figure 2.



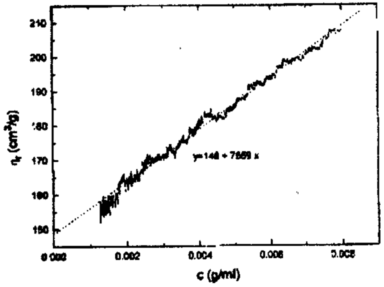
The analysis of the above raw data follows:

Analysis of Automated Data (PVP)

M_w=646,000g/mole, Rg=39nm,
A_2= 0.00035 cm^3-mole/g



- Intrinsic Viscosity= 148 cm^3/g

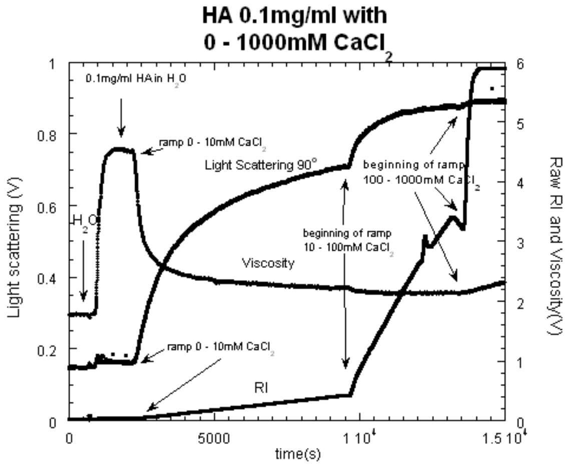


Automated determination of how polyelectrolyte dimensions, interactions and hyrdrodynamics respond to changing ionic strength.

Here, a programmable ternary mixing pump was used to pull a constant percentage of a stock polyelectrolyte (sodium hyaluronate) solution in pure water, while the second and third inputs were pure water and salt water reservoirs, used to form a continuous gradient of solvent ionic strength from pure water to 1M. The data look complex, but see the subsequent figure showing how the RI kept track of the salt, allowing all signals to be represented vs. salt concentration.

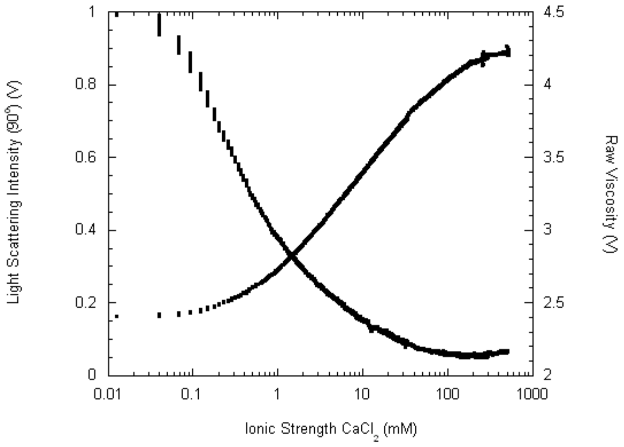
(from G.A. Sorci, W.F. Reed, Macromolecules, 37, 554-565, 2004)

Figure 1a



Below, the data from the above figure are plotted vs. ionic strength. The usual polyelectrolyte effects are seen; increase in scattering as electrostatic shielding leads to the decrease in A_2 and A_3, and the contraction of the polyelectrolyte coil, leading to decreased viscosity.

Figure 1b



The interpretation of this type of data in terms of Electrostatic Persistence Length (EPL) and Electrostatic Excluded Volume, and other theories can be found under the link to polyelectrolyte properties.

The following curves show how polyelectrolyte properties are sensitive to the valence and symmetry of added electrolyte, not just to the solution ionic strength. The theoretical interpretation and modeling is found in the reference.

(from G.A. Sorci, W.F. Reed, Macromolecules, 37, 554-565, 2004)

Figure 2a

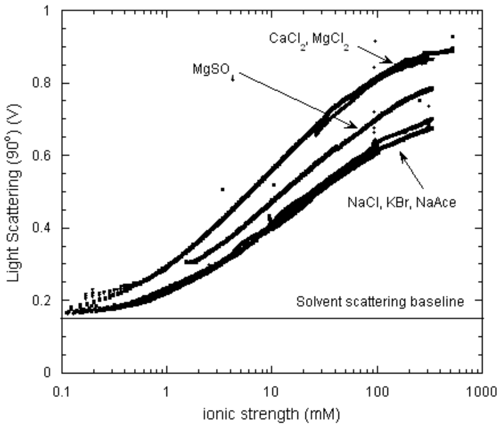
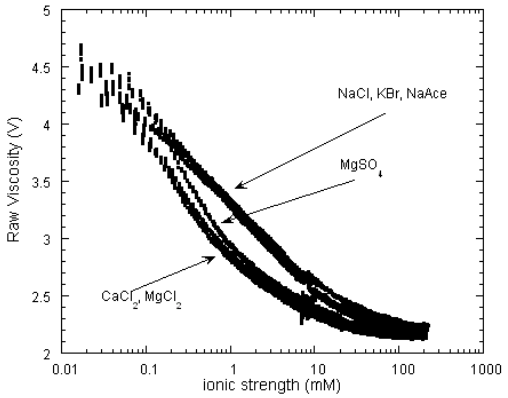


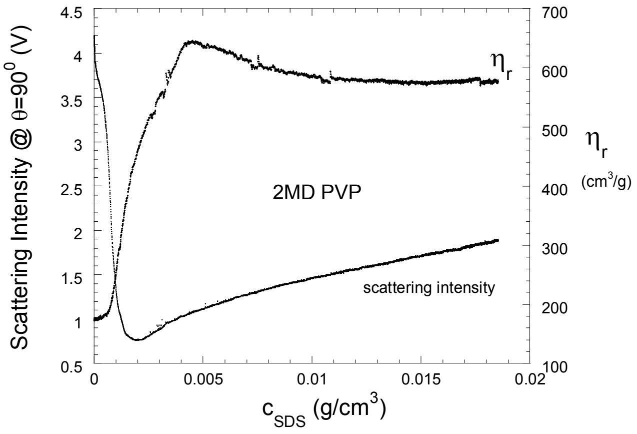
Figure 2b



Association of charged micelles with neutral polymers

The micelles were of sodium dodecyl sulfate, the polymers poly(vinylpyrrolidone). The figure below shows the remarkable scattering and viscosity behavior when fixed concentration PVP is titrated with SDS. The scattering *decreases* even though the mass of the polymers is increasing due to the association with SDS micelles, because the polymer becomes charged, a 'pseudopolyelectrolyte', and its A_2 increases dramatically, suppressing the light scattering. At the same time, the polymer dimensions increase, increasing the viscosity. A maximum is reached for both scattering and viscosity which is related to the concentration at which the PVP chains are saturated by SDS, and further addition of SDS merely adds to the solution ionic strength, hence shielding the anionic PVP/SDS complexes, leading to increasing scattering and decreasing viscosity.

(from G.A. Sorci, W.F. Reed, Langmuir, 18, 2, 353-364, 2002)



References to ACM

1. E. Bayly, J.L. Brousseau and W.F. Reed, "Continuous Monitoring of the Effect of Changing Solvent Conditions on Polyelectrolyte Conformations and Interactions", Int. J. of Polymer Characterization and Analysis, 7, 1-19, 2002

2. Gina A. Sorci and Wayne F. Reed, "Electrostatic and Association Phenomena in Aggregates of Polymers and Micelles", Langmuir, 18, 2, 353-364, 2002

3. Gina A. Sorci and Wayne F. Reed, "Electrostatically enhanced second and third virial coefficients, viscosity and interparticle correlations for linear polyelectrolytes", Macromolecules, 35, 13, 5218-5227, 2002

4. W. F. Reed, "Automatic, Continuous Mixing Techniques for Online Monitoring of Polymer Reactions and for the Determination of Equilibrium Properties", ch. 20, pp. 589-622, Handbook of Size Exclusion Chromatography and Related Techniques", 2nd Ed., Chi-san Wu, Ed., Marcel Dekker, 2003

5. Gina A. Sorci and Wayne F. Reed, "Effect of ion type and valence on polyelectrolyte conformations and interactions", Macromolecules, 37, 554-565, 2004