

Shouldn't it just be additive? Investigating how combined sugar and salt solutions influence a thermoresponsive polymer

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Osmolytes are a class of small organic molecules that influence the properties of macromolecules. First recognised for their function in osmotic pressure regulation in biological systems, they have since been identified as having a considerably wider role. Of particular note is their ability to denature and destabilise biomacromolecules. This destabilisation can occur via two paths: osmolytes interfere with the ability of the macromolecules to interact with, and be solvated by water molecules, or osmolytes interrupt hydrophobic interactions which are responsible for the formation of many biological structures. Sugars play many important roles in biological systems and, while it may not be their primary function, they also act as osmolytes. For example, glucose has been shown to destabilise synthetic macromolecules through osmolyte-type behaviour at elevated concentrations.¹ Specific ion effects which cannot be wholly explained by classical electrolyte theories, have also been found to significantly influence the properties of macromolecules. Traditionally, the variations observed between ions were attributed to their ability to “make” or “break” the structure of water. Upon further investigation it has been revealed that interfacial ion-partitioning plays a significant role in these specific ion effects where larger, less hydrated ions have an increased preference for interfacial regions.² These salt effects have been extensively investigated since they were first observed and generally follow a well-established series. We have previously shown that the concentration of an ion, and its position in this series, determines its ability to stabilise/destabilise macromolecules.³

As osmolytes and salts both play a significant role in a solution's ability to denature and destabilise biomacromolecules, their combined interactions (often present together in biological systems) are of particular interest in furthering our understanding. Herein, we investigate the combined effects of glucose and salts on the thermoresponse of Poly(*N*-isopropylacrylamide) (PNIPAM); a well characterised polymer that undergoes a temperature induced phase change at its lower critical solution temperature. Neutron reflectometry (NR) was employed to probe the internal structure and conformation of a PNIPAM brush while differential scanning calorimetry (DSC) examined the thermodynamic properties of free PNIPAM solutions (Fig. 1).

Keywords:

Osmolytes, Specific ion effects, PNIPAM, Neutron reflectometry, Differential scanning calorimetry

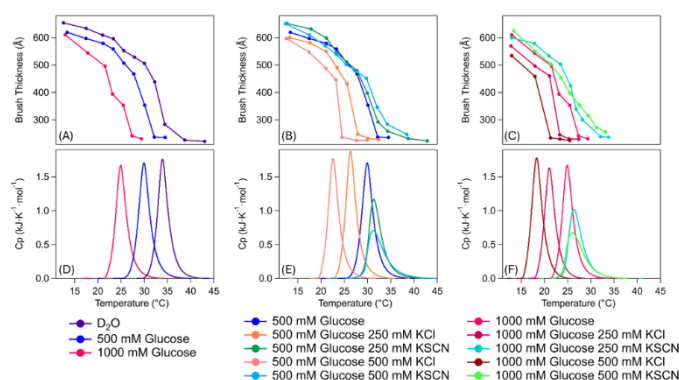


Figure 1. (A, B and C) PNIPAM brush thickness determined via NR and (D, E and F) specific heat capacity (C_p) of a PNIPAM solution measured with DSC as a function of glucose/salt concentration and temperature.

References:

¹ Edwin Johnson, Hayden Robertson, Erica Wanless, Grant Webber, Ben Humphreys, *Journal of Colloid and Interface Science*, **2025**. ² Pierandrea Nostro, Barry Ninham, *Chemical Reviews*, **2012**. ³ 17. Ben Humphreys, Erica Wanless, Grant Webber, *Journal of Colloid and Interface Science*, **2018**.