

Using NMR Relaxation to Study Adsorption Behavior in Mixed Polymer Systems

Scientists in cosmetics, paints and pharmaceuticals frequently utilize water-soluble neutral polymers such as poly(vinylpyrrolidone) (PVP) and poly(ethylene oxide) (PEO), alone and in combination, in their formulations. Understanding their adsorption behavior onto the surface of particles is a key to the preparation of stable dispersions and hence in obtaining optimum performance features.

The usefulness of NMR relaxation measurements to study the behavior of mixed polymer systems is illustrated below. Silicas are used extensively in a wide variety of applications. The two polymers, PVP and PEO, are known to adsorb onto silica but to different extents. In the graph, the relaxation rate ($1/\text{relaxation time}$) is plotted versus the silica-to-water ratio. The bottom red line shows the typical change in relaxation rate as a function of increasing silica particle concentration in water.

The blue line shows the effect of addition of a *fixed* quantity of PEO to each of the silica samples. There is an increase in slope (decrease in relaxation time) corresponding to polymer adsorption up to a silica-to-water ratio of approximately 0.06 after which the slope is the same as that for bare silica. PEO is continuously adsorbed from solution (as the total surface area of the dispersion is increased) until the polymer is depleted. Any new silica that is added is no longer coated with polymer and hence the slope reverts to that of bare silica. This plot is directly related to an adsorption isotherm for PEO on silica. The data for adsorption of PVP (green dotted line) shows similar behavior except that the breakpoint now occurs at a much lower silica-to-water ratio (ca 0.013) suggesting a much stronger affinity of the PVP for the silica surface compared to PEO. The final plot (black dotted line) shows the case where both PVP and PEO are added together. Here the data points at first follow the PVP adsorption plot, but after the PVP is exhausted then PEO can adsorb and the slope then parallels that for the PEO alone. This final plot is then a mixed adsorption isotherm showing preferential adsorption of PVP.

