Ionic liquids (ILs) are poised to replace conventional industrial fluids in a number of separation and reaction processes. In these applications, ILs offer improved solute selectivity, energy efficient recyclability, higher loading capacity, and reduced environmental toxicity in comparison to traditional organic solvents. However, engineering solute mass transport in ILs has been hindered by a lack of methods to observe it in operando that would provide better fundamental insight and rational design guidelines for solute-specific IL formulation. As a result, ILs are often selected from a vast design space of ionic components on the basis of their viscosity vis-à-vis the Stokes-Einstein relation, which assumes that solutes experience the IL as a continuum fluid. To overcome these limitations, we developed a new, label-free method, microfluidic Fabry-Perot interferometry (μFPI), to visualize solute diffusion in soft materials in situ. Here, we present several technologically-relevant demonstrations of μFPI to develop mechanistic understanding and quantitative models of transport limitations in ILs. In one case, experiments of water sorption into methylimidazolium ILs and ionogels reveal anomalous concentration-dependent solute diffusivities that violate the Stokes-Einstein relation. Instead, we find that water diffusion is accurately modeled by activated hopping between ion pairs. The magnitude of the activation barrier is quantitatively predicted by the strength of IL-solute hydrogen bonding, providing a direct molecular descriptor with which to engineer the diffusion of polar solutes in ILs. In a second example, studies of reactive CO2 absorption by amine-functionalized ILs provide detailed reaction-diffusion models for the sorption process, and identify material properties that are critical for determining the loading capacity of the IL. Overall, these examples show how μFPI can be used to develop and improve a priori diffusion models in complex liquids, help identify molecular interactions that control diffusion, and ultimately enable rational design of task-specific ILs.