

## Individual tuning of solvent parameters - From organic solvents to ionic liquids

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According to Marcus, solvent parameters have significant influence on the observed kinetics of electron transfer reactions [1]. Especially temperature dependent measurements, e.g. to get activation parameters, suffer a lot from these influences. So we tried to overcome all troubles with individual tuning of solvent parameters. Overall three different approaches have been started: First, changing viscosity at constant temperature keeping refractive index and dielectric constant stable. Secondly, changing dielectric constant at constant temperature keeping viscosity and refractive index stable. Last, keeping all parameters constant at variable temperatures. Basics and concepts for this tuning are presented in detail. Application to organic solvents: Electron transfer reaction experiments were performed under control of viscosity to identify diffusion dependent and independent reaction pathways [2]. With fine controlling of the dielectric constant it was possible to gradually switch between different reaction products depending on the stabilization of the ion pairs [3]. Very recently a solvent mixture with constant solvent parameters at different temperatures was also developed. Application to Ionic Liquids (ILs): Interpretation of activation parameters by means of EPR line broadening experiments in ILs lead to problems. In order to separate the diffusion from the temperature we decided to investigate a binary mixture of two ionic liquids. To keep the viscosity constant at variable temperatures different mixtures have been measured at a series of temperature values. The analysis yielded the temperatures of constant viscosity (here 30 cP). We have found a final proof that the concept of the experimental diffusion control works as expected [4].

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[1] for an overview see: G. Grampp, *Angew. Chem. Int. Ed. Engl.* 1993, 32, 691-693.

[2] A. Rosspointner, D. R. Kattnig, G. Angulo, S. Landgraf, G. Grampp, *Chemistry-A European Journal*, 2008, 14, 6213-6221; A. Rosspointner, D.R. Kattnig, G. Angulo, S. Landgraf, G. Grampp, A. Cuetos, *Chemistry-A European Journal*, 2007, 13(22), 6474-6483.

[3] S. Richert, A. Rosspointner, S. Landgraf, G. Grampp, E. Vauthey, D.R. Kattnig, *J. Am. Chem. Soc.* 2013, 135, 15144-15152

[4] J. Bächle, M. Berghold, S. Landgraf\*, G. Grampp, *ChemPhysChem*, 2017, 18, 1288-1292.