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High-Pressure Testing of Heterogeneous Charge Transfer in a Room-Temperature Ionic Liquid: Evidence for Solvent Dynamic Control

Tina D. Dolidze, Dimitri E. Khoshtariya, Peter Illner, Leszek Kulisiewicz, Antonio Delgado, and Rudi van Eldik

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Abstract

We report the first application of a high-pressure electrochemical strategy to study heterogeneous charge transfer (CT) in a room-temperature ionic liquid, [BMIM][BTA]. High-pressure kinetic studies on electron exchange for two redox couples of different charge type, viz. $[Fe(bipy)_3]^{3+/2+}$ and $[Fe(cp)_2]^{+/0}$, at bare Au electrodes within the range of 0.1–150 MPa, revealed large positive volumes of activation that were found to be virtually the same for the two redox couples in terms of the CT rate constants and diffusion coefficients, despite the reactant's charge type. Independent viscosity (fluidity) studies at elevated pressure (up to 175 MPa), were also performed and revealed a pressure coefficient closely resembling the former ones. Complementary temperature-dependent kinetic studies within the range of 298–358 K also revealed the virtual similarity in activation enthalpies for the same kinetic and diffusion processes, as well as the viscosity of [BMIM][BTA]. A rigorous analysis of the complete variety of obtained results strongly indicates that dynamic (frictional) control of CT is operative by way of the full adiabatic mechanism. The contribution of the Franck–Condon term to the activation free energy of the kinetic process seems almost diminished because of the high value of electronic coupling and freezing out of the outer-sphere reorganization energy. Further analyses indicate that frictional control most probably takes place through slow translational modes (implying “minimal volume” cooperative dislocations) of constituent ions. This kind of motion seems further slowed down within the vicinity of the active site presumably located within the diffusive-like zone situated next to the compact (first) part of the metal/ionic liquid junction.

† Inorganic Chemistry, University of Erlangen-Nürnberg.

‡ Institute of Molecular Biology and Biophysics.

§ Institute of Inorganic Chemistry and Electrochemistry.

* Corresponding authors. E-mail: dimitri.k@joker.ge(D.E.K.); vaneldik@ chemie.uni-erlangen.de (R.v.E.).

⊥ Institute of Fluid Mechanics, University of Erlangen-Nürnberg.

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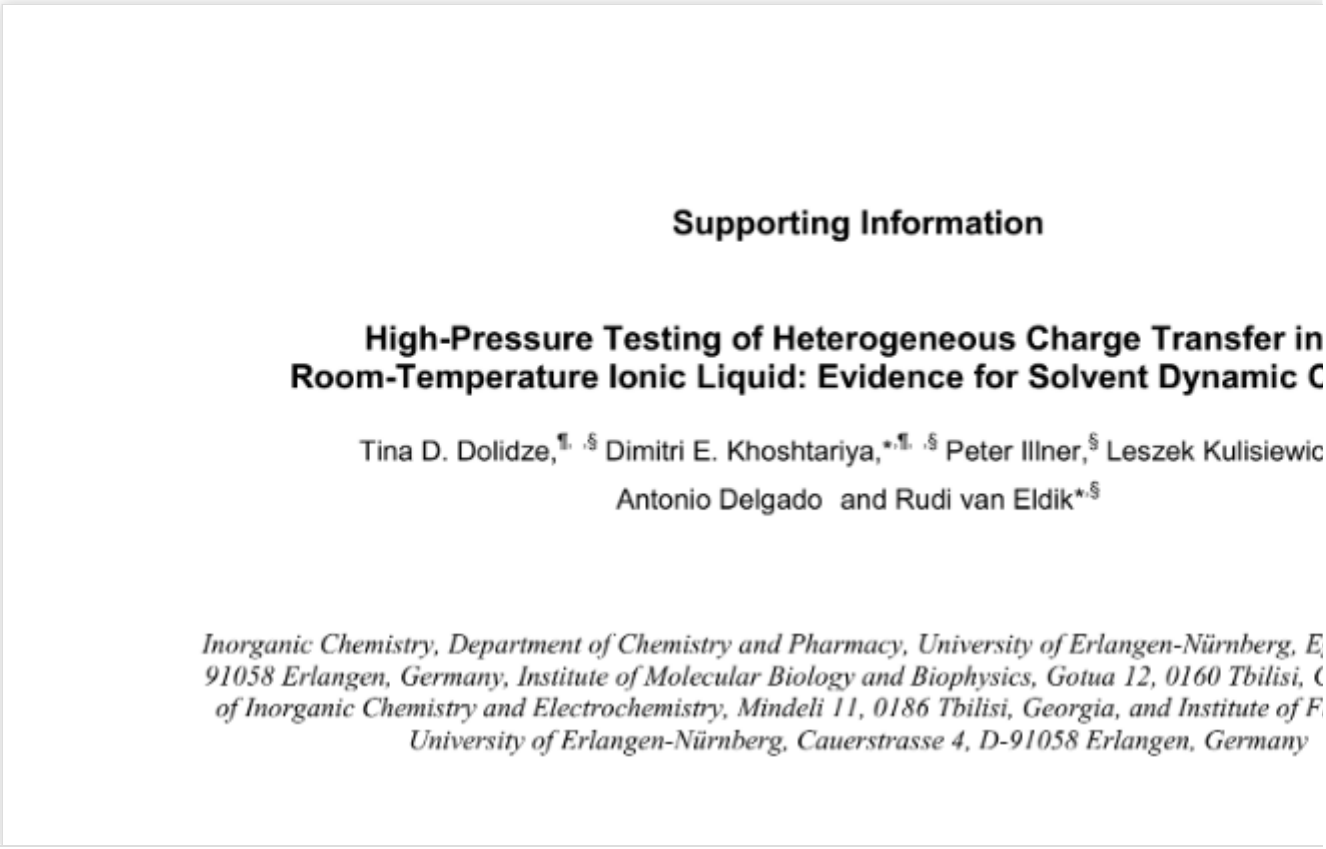

Supporting Information

High-Pressure Testing of Heterogeneous Charge Transfer in
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Tina D. Dolidze,[¶, §] Dimitri E. Khoshtariya,[*,¶, §] Peter Illner,[§] Leszek Kulisiewic
Antonio Delgado and Rudi van Eldik[*,§]

*Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, E
91058 Erlangen, Germany, Institute of Molecular Biology and Biophysics, Gotua 12, 0160 Tbilisi, G
of Inorganic Chemistry and Electrochemistry, Mindeli 11, 0186 Tbilisi, Georgia, and Institute of F
University of Erlangen-Nürnberg, Cauerstrasse 4, D-91058 Erlangen, Germany*

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