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ARTICLE

Are the Current Theories of Electron Transfer applicable to Reactions in Ionic Liquids? An ESR-Study on the TCNE/TCNE⁻• Couple

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Chemical reactivity is profoundly affected by solvent properties. Room temperature ionic liquids (RTILs) give rise to molecular environments that differ vastly from those established by molecular solvents of comparable macroscopic properties. In particular, charges are expected to be completely shielded in RTILs even though their dielectric constants are typically low. This raises the question whether electron transfer (ET) reactions in RTILs can be described in terms of Marcus' theory, a model which is fundamentally based on continuum dielectric theory. Here, we elucidate this question by studying a degenerate electron transfer process which, by design, is not affected by ambiguities in the driving force of the reaction and thus allows a clear-cut assessment of the ET activation energy. We report the rate constants and the activation parameters of the electron self-exchange reaction of the $\mathrm{TCNE}/\mathrm{TCNE}^{\bullet-}$ -couple in seven ionic liquids. Exchange rate constants range from $5.4 \cdot 10^7 \, \mathrm{M^{-1}s^{-1}}$ to $9.1 \cdot 10^8 \, \mathrm{M^{-1}s^{-1}}$ at 330 K; the activation energies vary from 14 kJ mol⁻¹ to 41 kJ mol⁻¹. The results are discussed in the framework of Marcus' theory. It is found that the solvent dependence of the rate constants cannot be described by the classical proportionality to the Pekar factor $\gamma = \left(1/n^2 - 1/\varepsilon_s\right)$.

Introduction

The advent in the research and application of room temperature ionic liquids (RTILs) has led a surge in interest in understanding the fundamental effects governing electron transfer (ET) reaction in these designer solvents. Various studies on heterogeneous (electrochemical) and homogeneous electron transfer reactions have recently reported on the kinetics of charge transfer reactions.[1-7] In comparison with molecular organic solvents of comparable macroscopic properties, remarkable differences in the rate constants and activation parameters have become apparent. Dynamical solvent effects, which give rise to the dependence of the ET rate constants on the longitudinal relaxation times of the solvent, have been considered.[5] Understanding the peculiarities of the reaction behaviour in RTILs is important for their wide-spread use in various applications, such as batteries, catalysis, etc. Here, we describe detailed investigations of the kinetics and the activation parameters of

the tetracyanoethylene ($\mathrm{TCNE}/\mathrm{TCNE}^{\bullet-}$) degenerate electron exchange (self-exchange) reaction in different ionic liquids. This redox couple is chosen because both its heterogeneous electrochemical and its homogeneous electron transfer in organic solvents have been studied in depth.[8-10] The heterogeneous rate constants have also been reported in ionic liquids.[11] In addition, the counter ion effect on the electron self-exchange in molecular solvents has been reported.[12] Here, we focus on the applicability of current theories of electron transfer, in particular on the role of the solvent-dependent outer-sphere reorganization energy, λ_o.

All existing theories based on Marcus theory subdivide the activation energy into two terms.[13-20] An inner-sphere contribution, λ_i, normally assumed to be independent of the solvent and an outer-sphere contribution, λ_o. λ_i accounts for the changes in molecular geometry accompanying the electron transfer. For the outer-sphere contribution, λ_o, a continuum solvent model is often employed, which results in the solvent dependence of the rate constant being governed by the refractive index, n, and the static dielectric constant, ε_s, via the Pekar factor $\gamma = \left(1/n^2 - 1/\varepsilon_s\right)$. Numerous experimental reports have demonstrated the validity of this model for both, heterogeneous and homogeneous electron transfer reactions in solution.[9,10,21,22] Owing to the fact that the derivation of λ_o is based on polarization effects, the question arises whether this concept is also applicable to ionic liquids.

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We focus on electron-self exchange reactions, because for this type of reaction no bonds are formed or broken and the free energy difference vanishes, $\Delta G^{\ne} = 0$ (as do all thermodynamic reaction parameters, e.g. $\Delta H^{\ne} = 0$, $\Delta V^{\ne} = 0$ and the equilibrium constant $K = 1$). As a consequence, the ambiguity related to the driving force of the reaction, which is often present in photo-induced electron transfer studies, is avoided and the governing electron transfer models simplify. In addition, conventional spectroscopic techniques are inapplicable. However, as the nuclear spin configurations may change upon electron transfer, ESR and NMR spectroscopy can be used to determine the electron transfer rate constant. Only a few papers describe the measurement of electron transfer rate constants in ionic liquids by dynamic ESR-spectroscopy.[2]

By contrast, there are several reports on the kinetics of photo-induced electron transfer (PET) reactions measured in ionic liquids. For intermolecular PET reactions quenching rate constants have been reported that exceed the diffusion rate constant estimated from viscosity.[23-25] Koch et al.[6] and Liang et al.[27] clearly pointed out that by correctly accounting for the static and transient stages of the quenching reactions, which are important in the high viscous ILs, intrinsic electron transfer rates slower than in conventional organic solvents result.[28] The dependence of the ET rate on the driving force of the ET reaction addressed by many authors: The Marcus Inverted Region (MIR) has been reported for some photo-induced electron transfer reaction occurring in ILs,[29-32] and in mixtures of ILs and conventional solvents such as methanol, 2-propanol and water.[31] The Rehm-Weller behaviour is found in several systems reaching the diffusion plateau.[25] Several ET-studies, both experimental and theoretical, indicate that the polarities of imidazolium-ILs are comparable to conventional solvents such as ethanol, acetonitrile etc.[33-36] For pyridinium-based ILs similar behaviours are found.[37] Only rarely have data for the total reorganization energy $\lambda = \lambda_i + \lambda_o$ been extracted by fitting the experimental Rehm-Weller[37] or MIR-curves. However, up to now no detailed investigations on the outer-sphere reorganization energies λ_o and their solvent dependence via the Pekar factor have been reported. There also exist some hints from electrochemically measured heterogeneous rate constants indicating that the outer-sphere Marcus behaviour is not obeyed in imidazolium ionic liquids.[38]

Experimental

Line-broadening effects measured by dynamic ESR-spectroscopy were used to obtain the rate constants of the electron transfer reactions. ESR-measurements were performed on a Bruker Elexsys E-500 X-band ESR-spectrometer equipped with a digital temperature control unit (Bruker). Temperatures were kept constant to within ±0.5 K. A microwave frequency of approximately 9.4 GHz was used. The field was modulated at 10 kHz with modulation amplitudes as low as 0.05 G, in accord with the extremely small peak-to-peak line-widths of the no-exchange spectra. A home written Matlab-program was used to simulate the ESR spectra. The program employs an approach similar to that reported in ref.

39. Tetracyanoethylene (Fluka, 97%) was sublimated before use. The oxygen sensitive radical anion $TCNE^{\bullet-}$ was generated by reduction with potassium iodide or tetrabutylammonium iodide under a nitrogen atmosphere using pre-degassed RTILs:

$$2\ TCNE + 2\ NBu_4^+I^- \longrightarrow 2\ TCNE^{-\bullet}NBu_4^+ + I_2$$
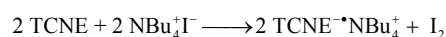
For all measurements the radical concentration was kept constant at $5 \cdot 10^{-4}$ M. Line-broadening effects were observed by adding the diamagnetic precursor, $TCNE$, at different concentration, up to 62 mM. Ionic liquids, butylmethylimidazolium hexafluorophospate (bmimPF$_6$, >99,5%), butylmethylimidazolium tetrafluoroborate (bmimBF$_4$, >99,5%), 1-methyl-3-octylimidazolium hexafluorophosphate (omimPF$_6$, >99%), 1-methyl-3-octylimidazolium tetrafluoroborate (omimBF$_4$, >99%), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (emimTfN, >99%), 1-methyl-3-butylimidazoliumbis(trifluoromethylsulfonyl)imide (bmimTfN) and 1-n-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (hmimTfN, >99%) were purchased from Ionic Liquids Technologies (Io-Li-Tec), Germany, and dried for 24 hours under high vacuum (>10^{-6} Torr) at 40°C to remove residual water. For some of the ILs purification by column chromatography over aluminium oxide (Fluka, type 504c acidic) was necessary prior to the drying procedure in order to remove impurities (most likely free amines), which were observed to reduce TCNE even in the absence of iodides. The dried ILs were stored under a nitrogen atmosphere in Schlenk tubes, which were kept in a desiccator over P$_4$O$_{10}$ and in the dark. All samples were transferred into capillaries of 0.8 mm inner diameter and, after additional degassing by several freeze-pump-thaw cycles, sealed off in vacuum. In order to complement one of our earlier papers[9], we have also conducted comparative measurements in classical organic solvents.

Results and Discussion

Temperature dependence of the nitrogen hyperfine coupling constants

For the less viscous ionic liquids emimTfN, bmimTfN, hmimTfN and bmimBf$_4$, the nitrogen hyperfine coupling constant of the $TCNE^{\bullet-}$ radical anion at 300 K is 0.157 mT, in agreement with the literature value measured in N,N-dimethylformamide.[40] For the more viscous ionic liquids bmimPF$_6$, omimPF$_6$ and omimBF$_4$ this value is slightly larger, 0.159 mT. Figure 1 shows the temperature dependence of the nitrogen coupling constants for the reported ionic liquids; the temperature coefficients are summarized in Table 1.
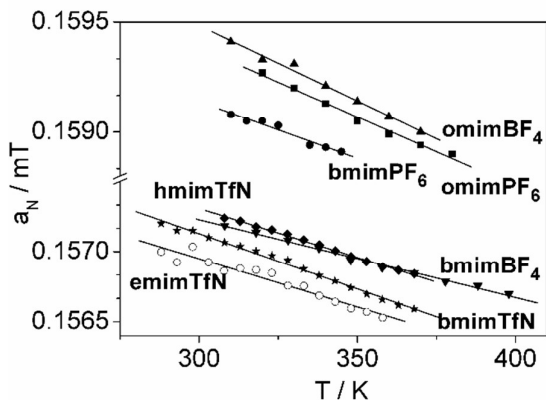
Fig.1: Temperature dependence of the nitrogen coupling constants, a_N, for $TCNE^{\bullet-}$ in the studied ionic liquids.

Table 1: Temperature coefficients da_N/dT and nitrogen hyperfine coupling constants, a_N, at 300 K for $TCNE^{-\bullet}$ in the ionic liquids.
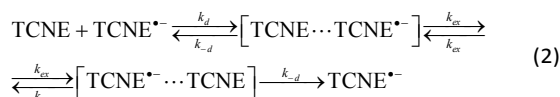
Ionici liquid	da_N/dT x 10^{-6} mT K^{-1}	a_N / 300 K mT
omimBF$_4$	-6.960 ± 0.31	0.1595
bmimPF$_6$	-5.16 ± 0.46	0.1591
bmimBF$_4$	-5.55 ± 0.17	0.1572
omimPF$_6$	-6.32 ± 0.30	0.1594
bmimNtF	-7.89 ± 0.17	0.1571
emimNtF	-6.87 ± 0.50	0.1569
hmimNTf	-7.00 ± 0.13	0.1573

Electron-self exchange kinetics

The overall reaction,

$$TCNE + TCNE^{\bullet-} \xrightleftharpoons[k_{obs}]{k_{obs}} TCNE^{\bullet-} + TCNE , \qquad (1)$$
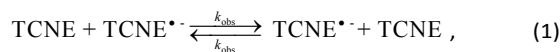
involves the diffusive formation of an encounter complex, the elementary electron transfer event, and the dissociation of the successor complex:

$$TCNE + TCNE^{\bullet-} \xrightleftharpoons[k_{-d}]{k_{d}} \left[TCNE \cdots TCNE^{\bullet-}\right] \xrightleftharpoons[k_{ex}]{k_{ex}}$$
$$\xrightleftharpoons[k_{ex}]{k_{ex}} \left[TCNE^{\bullet-} \cdots TCNE\right] \xrightarrow{k_{-d}} TCNE^{\bullet-} \qquad (2)$$

Above, the reactions have been labelled by their associated rate constants. The exchange frequency v_{ex} is extracted from computer simulations of the experimental ESR-spectra. All spectral parameters for the simulation are obtained from the no-exchange spectra ($[TCNE] \approx 0$ mM), the only adjustable parameter in this process being the exchange frequency v_{ex}.

k_{obs} is found from the linear regressions of $v_{ex} = k_{obs}[TCNE]$ versus $[TCNE]$ of measurements at typically 7 different concentrations. Figure 2 shows a typical line-broadening experiment in bmimPF$_6$ at 350K for which the concentration of neutral TCNE was increased up to 62 mM. Figure 3 shows a corresponding plot of the combined exchange frequencies at various temperatures and concentration, from which the temperature dependent k_{obs} s have been extracted.
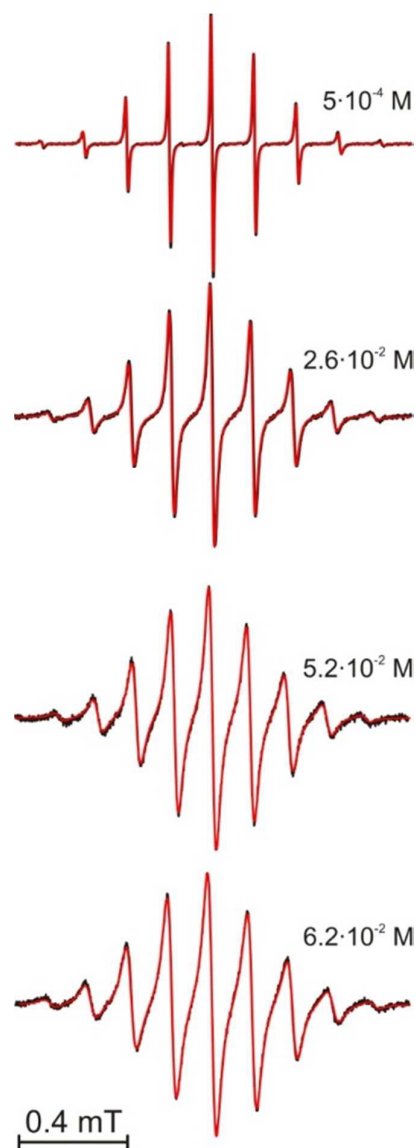
Fig. 2: ESR-line-broadening (black experimental and red simulated spectra) for the $TCNE/TCNE^{\bullet-}$ redox system in bmimPF$_6$ at T=350K.
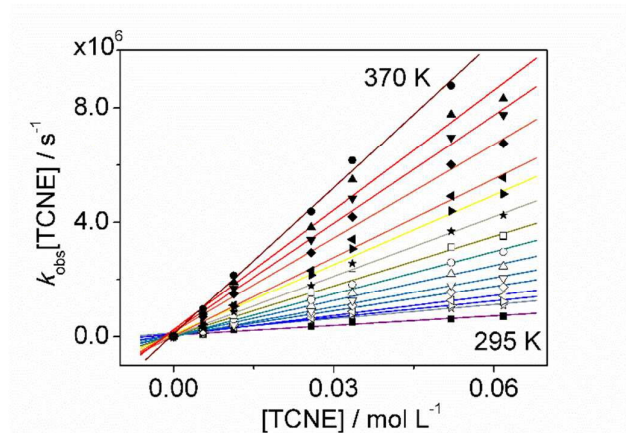

Fig. 3: Linear dependence of $k_{obs}[TCNE]$ on $[TCNE]$ in bmimPF$_6$ at different temperatures.

The encounter pre-equilibrium model, eq. (2) accounts for the aforementioned diffusion effects on the electron transfer reaction by:

$$\frac{1}{k_{obs}} = \frac{2}{k_d} + \frac{1}{k_{et}},\qquad(3)$$

where k_d denotes the diffusion rate constant. In the absence of Coulombic interactions between the reactants (as TCNE is uncharged), k_d can be expressed as $k_d = \frac{8RT}{3\eta}$. Using the association constant $K_A = k_d/k_{-d}$, the electron transfer rate is related to electron exchange rate k_{ex} between the precursor and the successor complex by $k_{et} = K_A k_{ex}$ (see eq. (2)). Table 2 lists the ET rate constants at 298 K and 330 K together with the dielectric properties and the Pekar factors of the studied solvents. We have compared the rate constants for the ILs with those observed in the molecular solvents acetonitrile (CH$_3$CN), propylene carbonate (PC), dichloromethane (CH$_2$Cl$_2$), chloroform (CH$_3$Cl), benzonitrile (BN), bromobenzene (PhBr), ethanol (EtOH) and isopropanol (iPrOH). Despite considerably larger viscosities (and thus smaller diffusion rate constants and overall rate constants, k_{obs}), the rate constants of the elementary ET are comparable to those observed in EtOH or iPrOH.

Table 2: Refractive indices squared, n^2, static dielectric constants, ε_s, Pekar factors, γ, and rate constants of degenerate electron exchange, k_{et}, in M^{-1}s^{-1}, at 298 K and 330K for the studied solvents.

Solvent	n^2 298K	ε_s 298K	γ 298 K	$k_{et} 10^8$ 298 K	$k_{et} 10^8$ 330 K
emimTfN	2.022	12.25 [41]	0.41	1.83	9.1 ± 0.5
bmimTfN	2.036	13.7 [42]	0.43	1.62	6.4 ± 0.4
hmimTfN	2.046 [50,51]	12.7 [43]	0.41	0.90	4.4 ± 0.2
bmimBF$_4$	2.021 [49]	14.6 [43]	0.43	0.24	0.9 ± 0.1
bmimPF$_6$	1.986	16.1 [43]	0.44	1.39	2.6 ± 0.1
omimBF$_4$	2.051 [44]	7.5 [48]	0.35	-	0.5 ± 0.1
omimPF$_6$	2.025 [45]	9.7 [48]	0.38	-	0.8 ± 0.1
CH$_3$CN	1.807 [9a]	35.9 [9a]	0.53 [9a]	29.1 [a]	45.7 [a]
PC	2.021 [9a]	64.9 [9a]	0.48 [9a]	4.7 [a]	9.3 [a]
CH$_2$Cl$_2$	2.028 [9a]	8.9 [9a]	0.38 [9a]	53.5 [a]	84.9 [a]
CHCl$_3$	2.091 [9a]	4.8 [9a]	0.27 [9a]	58.9 [a]	90.3 [a]
BN	2.335 [9a]	25.2 [9a]	0.39 [9a]	15.30	-
PhBr	2.424 [9a]	5.4 [9a]	0.23 [9a]	16.0 [a]	26.1 [a]
EtOH	1.848	24.47 [46]	0.50	1.44	-
iPrOH	1.897	19.34 [47]	0.48	1.20	-

a) PhD-thesis W. Harrer, University of Erlangen, Germany, 1986.

Arrhenius plots of ln(k$_{et}$) versus $1/T$, given in Figure 4, show straight lines resulting in the activation parameters listed in Table 3.
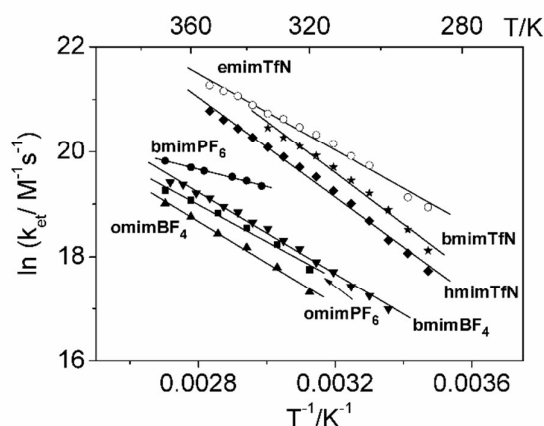
Fig. 4 Plot of $\ln(k_{et})$ versus $1/T$ for the $TCNE/TCNE^{\bullet-}$ redox couple in different ionic liquids.

Table 3: Viscosities of the solvents, energy of the solvent, experimental activation energies, ΔG_{exp} and solvent reorganization λ_o energies in kJ mol^{-1}. λ_o(IL) has been calculated from eq. (12) and λ_o(Marcus) from eq. (6).

Solvent	η /cP	H_η	ΔG_{exp}	λ_o	λ_o	λ_o

	298K	kJ/mol	kJ/mol	exp. [a]	IL	Marcus
emimTfN	32.9	23.5	30.3	53.3	15.2	55.1
bmimTfN	53.4	28.0	40.7	79.3	14.2	55.8
hmimTfN	68.8	29.4	39.6	68.5	13.5	54.7
bmimBF$_4$	104.4	30.1	32.3	30.3	23.1	56.9
bmimPF$_6$	283.1	34.0	13.7	-	19.9	58.9
omimBF$_4$	344.7	38.2	38.2	15.6	18.9	47.2
omimPF$_6$	742.8	44.5	24.2	-	16.8	50.7
CH$_3$CN	0.3	5.5	12.2	52.8	-	69.4
PC	2.5	11.1	17.5	51.4	-	64.0
CH$_2$Cl$_2$	0.4	6.9	12.4	47.1	-	50.7
CHCl$_3$	0.6	6.8	11.0	40.8	-	36.0
PhBr	1.13	9.1	13.2	39.9	-	30.7

[a] calculated from: $\Delta G^*_{exp} = H_\eta + \dfrac{\lambda_i + \lambda_o}{4} - V_{PS} + \dfrac{V^2}{\lambda_i + \lambda_o}$ using λ_i for 295 K.

Following Marcus' Theory, the activation free energy of degenerate electron exchange, ΔG^*, is equal to

$$\Delta G^* = \frac{\lambda}{4} - V + \frac{V^2}{\lambda}, \tag{4}$$

which applies to the diabatic as well as to the adiabatic region with $V > RT$. Kochi et al. have studied the charge-transfer absorption of the $\left[TCNE \cdots TCNE^- \right]$-precursor complex in the framework of Marcus-Hush theory. The authors suggest a remarkable resonance splitting energy of V = 11.9 kJ/mol, suggesting that the ET classifies as Robin-Day Class II. V is furthermore solvent independent[51]. As mentioned above, λ is the total reorganisation energy, which comprises contribution from changes in the internal structure of the reactants and the polarization of the solvent. According to the Holstein model, which accounts for the temperature dependence of nuclear tunnelling, the inner-sphere reorganisation energy, λ_i, is given by

$$\lambda_i(T) = \lambda_i^\infty \left(\frac{4 k_B T}{h\nu_i} \tanh \frac{h\nu_i}{4 k_B T} \right), \tag{5}$$

where λ_i^∞ is the inner sphere reorganization energy in the high-temperature limit for which nuclear tunnelling is negligible.[52a] ν_i is the mean vibration frequency, for which a value of 1650 cm^{-1} has been used below. Recently, Li et al.[52b-d] pointed out that constrained density functional theory (CDFT) calculations for the $TCNE^{\bullet-}$ reveal an interesting out-of-plane distortion of the four equivalent cyano-groups by an angle of 10.1° in good agreement with crystallographic data. The corresponding $\lambda_i^\infty / 4$ is 3.25 kJ mol^{-1}.

The polarization of the solvent molecules surrounding the reactants gives rise to the outer-sphere reorganisation energy, which according to Marcus' theory is given by

$$\lambda_o = \frac{e_0^2 N_L}{4\pi\varepsilon_0} g(r,d) \gamma. \tag{6}$$

The parameter γ in eq. (6) is the Pekar factor, which subsumes the dependency on the solvent properties:

$$\gamma = \left(1/n^2 - 1/\varepsilon_s \right). \tag{7}$$

The geometrical term, $g(r,d)$ is a function of the geometry of the reactants and the precursor complex. For spherical reactants it is a simple function of the effective molecular radius, r, and the reaction distance, d. For the redox couple $TCNE / TCNE^{\bullet-}$, $g(r,d)$ has been experimentally found to be $9.8 \cdot 10^8$ m^{-1}.[9a] This value is used in the calculations discussed below. λ_o is deduced from the change in the dielectric polarization using the thermodynamic procedure that Gibbs energy changes can be calculated from the reversible work done along a hypothetical path, using a non-equilibrium dielectric polarization description.[17] Here, the fast induced polarization is accounted for by n^2 and the total polarization including the slow polarization by ε_s. Weingartner [53] argued that the dipole moment is an "ill-defined" quantity in ionic liquids consisting of charged ions. That does not consequently mean ionic liquids do not exhibit dielectric constants, although for ILs these physical properties cannot be obtained from conventional measurements. Buchner et al [54] pointed out that it is possible to obtain ε_s-values from dielectric response spectroscopy employing a wide range of frequencies. In addition, ε_s-values have been reported using solvatochromic UV-VIS-absorption shifts and the fluorescence of probe dyes.[55] The ε_s-values reported are in the range of 13-16. It is still questionable whether an orientation polarization part based on ε_s can be included in the Pekar factor, because no solvent dipole reorientation is expected to occur in ionic liquids. In this limit, it is expected that $n^2 \approx \varepsilon_s$ and the outer-sphere reorganization energy vanishes. This model was recently applied to the self-exchange reaction of methyl viologen in ILs.[2] In any case, λ_o is expected to vary little among different ionic liquids. Direct application of eq. (6), suggests λ_o-values ranging from 48 to 59 kJ/mol for the ILs studied here.

Recently, a theoretical calculation of the reorganization energy in ILs was published by Xiao and Song.[58] Calculations were done under the non-linear response approximation using Debye-Hückel theory. The authors gave an analytical equation for λ_o including these effects

$$\lambda_o = \frac{e^2 N_L}{4\pi\varepsilon_0} \left\{ \left(\frac{1}{n^2} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{r} - \frac{1}{d} \right) + \frac{1}{\varepsilon_s} \left(\frac{2\kappa}{1+\kappa r} \right) + \frac{1}{d\varepsilon_s} \left(\frac{e^{-\kappa(d-r)}}{1+\kappa r} - 2 \right) \right\} \tag{8}$$

$$\lambda_o = \frac{e^2 N_L}{8\pi\varepsilon_0 n^2} \left\{ \frac{2\kappa}{1+\kappa r} + \frac{1}{d} \left(\frac{2 e^{-\kappa(d-r)}}{1+\kappa r} - 2 \right) \right\}. \tag{9}$$

κ denotes the inverse Debye length $\left(\varepsilon_0 n^2 k_B T / 2 e_0^2 N_L \right)^{-1}$. Equation (8) takes into account solvent contributions from dipoles, ions and induced dipole-ion interactions. For weak interactions, $\kappa \to 0$, the classical Marcus equation ensues, while in the ionic liquid case no

dipole species are involved so that $n^2 \approx \varepsilon_s$ and eq.(9) remain for that case. Table 3 lists values of λ_o (IL) calculated from eq. (9). A detailed discussion about non-linear response effects can also be found by Zhou and Szabo.[59] A similar theory of the effect of spatial correlation in solvent polarization fluctuations on the character of screening in electrolyte solutions was discussed by Kornyshev.[60]

The degenerate electron exchange of TCNE in conventional organic solvents is characterized by a solvent dynamical effect, which gives rise to the dependency of the rate constant on the solvent longitudinal relaxation time and the Pekar factor γ [9]. While γ varies from 0.05 to 0.53 for the studied organic solvents, the Pekar factor for the ionic liquids is nearly constant. However, the rate constants vary between 5.4 to $91 \cdot 10^7$ M^{-1}s^{-1}, suggesting that solvent-friction does play a role. Based on Kramers' theory, Goldanskii pointed out that in the limit of large viscosities the rate expression is given by:

$$k_{et} = K_A \frac{A}{\eta} \exp\left(-\frac{\Delta G^*}{RT}\right) \qquad (10)$$

As can be seen from Table 3 the viscosities of the ionic liquids are large and fulfil the criteria of Goldanskii[56] and Kramers[57] theory. The pre-exponential factor A does not (strongly) depend on the temperature. Assuming a temperature dependence of the viscosity of the form

$$\eta = \eta_0 \exp\left(\frac{H_\eta}{RT}\right), \qquad (11)$$

one gets the following expression for the activation energy

$$\Delta G^*_{\exp} = H_\eta + \frac{\lambda_i + \lambda_o}{4} - V_{PS} + \frac{V^2}{\lambda_i + \lambda_o} \qquad (12)$$

It is noted that the temperature dependence of the electron transfer rate constant is in general complex with many parameters in the pre-exponential factor and the activation energy depending on temperature. However, except for the scenario of Kramers' theory or the more specific solvent friction to be discussed below, the temperature dependence of the pre-exponential factor is weak (e.g. linear or sub-linear in T) and can in good approximation be neglected when comparing activation energies. Furthermore, within the temperature ranges studied here, the temperature-dependence of the reorganization energy is negligible. These suppositions are in agreement with the finding of linear Arrhenius plots (see Figure 4).

We have used eq. (10) to evaluate the experimental solvent reorganization energies from the experimental activation energies as summarized in Table 3. In molecular solvents the activation energies predicted by Marcus theory, eqs. (4) and (6), agree favourably with the experimental findings. For the ionic liquids, the experimental reorganization energy depends markedly on the ionic liquids, which is at odds with the comparably constant reorganization energy predicted by both models, eq. (6) and (9). The low-viscosity ILs exhibit outer-sphere reorganization energies close to or even exceeding the Marcus model. On the contrary, for omimBF$_4$, λ_o is closer to the prediction of eq. (9) and significantly smaller than the Marcus estimation. For bmimPF$_6$ and omimPF$_6$, the

activation energy is smaller than H$_\eta$, suggesting that the ET activation energy and thus λ_o is close to zero. It is interesting to note that both these ILs are known to form microstructures. The full equation (8) also does not fit the experimental λ_o-values. In particular, none of the models is able to account for the dependence of the reorganization energy on the identity of the IL.

We have also focused on the IL-dependence of the rate constants at 298 K. A solvent dependence according to Marcus Theory should be expressed through the Pekar factor γ. According to classical Marcus theory $\ln(k_{et})$ is expected to linearly depend on γ. On the other hand, for the solvent dynamical regime the ET rate constants can be modelled by

$$k_{et} = \frac{1}{\tau_L} \sqrt{\frac{\lambda_o}{16\pi k_B T}} \exp\left(-\frac{\lambda^2}{4\lambda_o k_B T}\right) \dots \qquad (13)$$

suggesting $\ln\left(k_{et}\tau_L\gamma^{-1/2}\right)$ vs. γ yields a linear correlation. For TCNE in ILs, neither a linear correlation of $\ln(k_{et})$ versus γ, nor the classical Marcusian behaviour, nor the solvent dynamical expression appear to hold. Figure 5 gives the latter plot for molecular solvents and ionic liquids. Due to the lack of relaxation data for ionic liquids, we have approximated the longitudinal relaxation time τ_L by the viscosity η using the Debye equation $\tau_L = \left(n^2 / \varepsilon_s\right)\left(3V_m\eta / RT\right)$. Therefore, we conclude that there is no γ-dependence of the electron transfer rate constants in ionic liquids. Contrary to this, but in accordance with our previous findings[9], in other conventional organic solvents the TCNE/TCNE$^{\bullet-}$-couple shows a solvent dynamical effect expressed by the solvent longitudinal relaxation times. The alcohols are omitted from Figure 5, because as non-Debye solvent they exhibit three different relaxation times requiring a more complex analysis. This finding is in contrast with data for heterogeneous electrochemical electron transfer reactions of ferrocene in ionic liquids, for which a τ_L-influence has been observed.[5]
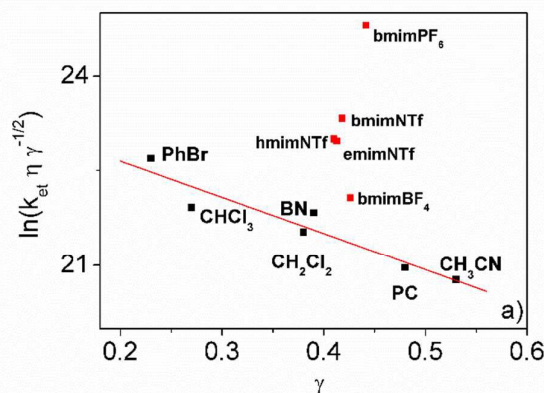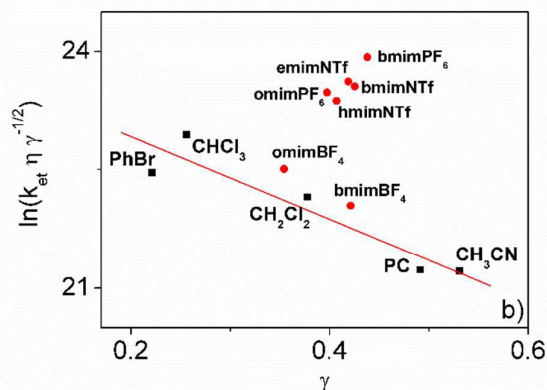
Fig. 5 Solvent dependence of the TCNE/TCNE$^{.-}$-couple in different conventional organic solvents and in various ionic liquids, according to eq. 11 for a) 298 K and b) 330 K.

Conclusions

From the kinetics and the activation parameters of the $TCNE/TCNE^{.-}$ couple it is shown that the solvent dependent outer-sphere reorganization energy λ_o cannot in general be explained in the framework of the classical Marcus dependence on the Pekar factor γ. The experimental activation energies are interpreted with contributions from the inner-sphere reorganization energy λ_i, the energy H_η related to the temperature dependence of the viscosity of the ionic liquids and the resonance splitting energy V. The experimental outer-sphere reorganization λ_o cannot be explained by Marcus theory and the recent theory by Xiao and Song.[58]

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