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# An old reaction in new media: kinetic study of a platinum(II) substitution reaction in ionic liquids†

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We report the kinetic study of the substitution reaction of a cationic platinum(II) complex $[Pt(dpma)Cl]^+$ (dpma ≡ di(2-picolyl)amine) with thioacetate in room temperature ionic liquids {$[C_4C_1im][NTf_2]$, $[C_4C_1py][NTf_2]$, $[C_4C_1py][OTf]$ and $[(C_3O)C_1im][NTf_2]$} and molecular solvents (water, methanol and DMSO). The reaction was studied as a function of the nucleophile concentration and temperature, under pseudo-first order kinetics. The reaction follows an associative mechanism with a two-term rate law, both in the studied ionic liquids and molecular solvents. It was found that the reaction rate was higher in water, followed by the ionic liquids and DMSO and then methanol. The solvent effect on this reaction was examined using a linear solvation energy relationship based on the Kamlet–Taft solvent scale ($\alpha$, $\beta$, and $\pi^*$). The bimolecular reaction rate increases with increasing hydrogen bond donor ability ($\alpha$) and dipolarity/polarizability ($\pi^*$) of the solvent. The activation parameters $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ were estimated in each solvent and showed that the mechanism is the same in all solvents. No 'ionic liquid effect' was found for this reaction, since the reaction rates are found to be within the range observed in molecular solvents and described by the polarity parameters.

## Introduction

Ionic liquids have been used as solvents for organic, inorganic, organometallic, and transition metal catalysed transformations.[1,2] They have also found large-scale industrial application in the BASIL process.[3,4] Our group has a considerable programme of quantitative investigation of the effect of ionic liquids on the nucleophilicity towards carbon of a range of nucleophiles.[5–9] It was concluded that a pure Hughes–Ingold view of the system was not sufficient, as hydrogen-bonding interactions were often the dominant solvent–solute effects governing the behaviour of the system. Instead, a Kamlet–Taft linear solvation energy relationship (LSER)[10] approach was utilized to effectively describe the solvent effects on these nucleophilic reactions.

The synthetic flexibility of transition metal complexes provides the opportunity to investigate how ionic liquids interact with different electrophiles to affect their reactivities. Platinum(II) complexes usually undergo ligand substitution by associative mechanisms, and only rarely dissociatively.[11] For associative reactions, a two-term rate law usually emerges, indicating competing paths in which the substrate is attacked first by either the incoming ligand or a solvent molecule, or in our case ion. In molecular systems, the parallel participation of the "solvent path" has allowed development of linear free energy-based scales of nucleophilic reactivity for incoming groups, which is the most influential kinetic control but is, unsurprisingly, appreciably different from that associated with carbon centres.

Only a few reports are found in the literature concerning platinum substitution reactions in ionic liquids,[12–15] two of them with $[Pt(terpy)Cl]^+$ and the other with $[Pt(apa)Cl]^+$ [15] as substrates (terpy = 2,2′,6′,2″-terpyridyl, apa = 2,6-bis(aminomethyl)pyridine) and thiourea or iodide as nucleophiles. The mechanism in ionic liquids was found to have an associative nature as in molecular solvents, but the authors were unable to find a correlation with the solvent polarity. The same group also reported studies on the influence of the molecular solvents in the substitution reaction of cationic platinum complexes with thiourea,[16] including the complex reported here. Our results are the first example of the application of Kamlet–Taft LSER to describe the solvent effects on a platinum substitution reaction. We were also able to find a suitable correlation for some of the results referenced above,[16] which will be compared with ours.

## Experimental

### Materials and reagents

All chemicals used were of analytical reagent grade. 1-Methylimidazole and 1-methylpyrrolidine were purchased from Acros Organics and distilled from potassium hydroxide; 1-chlorobutane was purchased from Acros Organics and distilled from phosphorus pentoxide. Lithium bis(trifluoromethylsulfonyl)imide {$Li[NTf_2]$} and lithium trifluoromethanesulfonate {Li[OTf]}were purchased from Apollo Scientific and used as received. Di(2-picolyl)amine and potassium thioacetate were obtained from Sigma-Aldrich and Acros Organics, respectively. The molecular solvents were either dried by standard procedures or obtained anhydrous from Sigma-Aldrich. Syntheses of the ionic liquids were performed under anaerobic conditions using standard Schlenk techniques. The preparations and spectral data of the ionic liquids have been described elsewhere[17] and are reported in

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† Electronic supplementary information (ESI) available: Characterization of the ionic liquids; Plots of $k_{obs}$ ($s^{-1}$) *vs.* [nucleophile] ($M^{-1}$) and Eyring plots. See DOI: 10.1039/b822152a

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the ESI.† The procedure used in its preparation and purification afforded colourless liquids, suitable for spectroscopic studies. They were used in the preparation of stock solutions of the platinum complex and nucleophile.

### Instruments

$^1$H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Positive and negative ESI and FAB mass spectra were recorded on a VG AutoSpec-Q mass spectrometer. UV-vis spectra were recorded on a Perkin-Elmer UV-visible Lambda 25 spectrophotometer. A thermostatic water circulator controlled the sample-holder temperature.

### Synthesis of [Pt(dpma)Cl]Cl

*Cis/trans*-$Pt(Me_2S)_2Cl_2$ was synthesized according to a literature procedure.[18] Di(2-picolyl)amine (dpma, 0.20 g, 1 mmol) dissolved in methanol (5 mL) was added to a solution of *cis/trans*-$Pt(Me_2S)_2Cl_2$ (0.36 g, 1 mmol) in refluxing methanol (10 mL). Over a period of minutes the yellow product precipitated and after cooling to room temperature and addition of diethyl ether (50 mL) it was filtered, washed with diethyl ether and dried under vacuum. Since the $^1$H NMR spectrum showed the presence of impurities the product was recrystallised from hot water and orange crystals were obtained. Yield: 30% Analysis Calcd. for $C_{12}H_{13}N_3Cl_2Pt{\cdot}2H_2O$: C, 28.8; H, 3.42; N, 8.4; Found: C, 28.9; H, 3.1; N, 8.7%. *m/z* (FAB+): 430 {[Pt(dpma)Cl]$^+$, 100%}, 860 {[Pt(dpma)Cl]$_2^+$ 10%}.

### Kinetic studies

The complex and nucleophile stock solutions were prepared by weighing the reactants and introducing them in volumetric flasks, which were then sealed, purged with $N_2$ and filled with the solvent under investigation (freshly degassed *in vacuum*). Quartz cuvettes were also sealed and purged with nitrogen before adding the reactants. Accurate aliquots of the reagents were added to the cuvettes with Hamilton gastight® volumetric syringes. The displacement of chloride by thioacetate from [Pt(dpma)Cl]Cl was initiated by adding 50 μL of a stock solution of [Pt(dmpa)Cl]Cl (*ca.* $2 \times 10^{-3}$ M) in the studied solvent, to a solution of potassium thioacetate (KSAc) previously brought to the reaction temperature (10 min) in a thermostatic cell in the spectrophotometer. The concentration of the nucleophile was always large enough to provide pseudo-first order kinetics (at least a 10-fold excess). After preliminary scans to determine spectral changes and the influence of variable ionic strength (in the case of the molecular solvents), the spectra were measured between 240 and 360 nm and the ionic strength (in molecular solvents) was set to 0.01 M ($LiClO_4$). A 0.002 M solution of LiCl was used to prepare the platinum stock solutions in molecular solvents, in order to avoid solvolysis of the complex. The second–order rate constants were corrected with the Debye–Hückel equation: $\log \gamma = -AZ^2I^{1/2}$ and $A = 1.82 \times 10^6 (\varepsilon T)^{-3/2}$.

Pseudo-first order rate constants ($k_{obs}$) were obtained by a non-linear least-squares fit[19] of the experimental data to $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where $A_0$ and $A_\infty$ are the absorbance after mixing of the reagents and after completion of the reaction, respectively. All reactions were monitored at 290 nm and all reported rate constants are the average of at least three kinetic runs under each experimental condition. The activation parameters were determined from temperature studies over the range 20–40 °C.

## Results and discussion

### Reactivity

The kinetic study of the ligand substitution reaction of Pt(dpma)Cl$^+$ with thioacetate was performed in molecular solvents and ionic liquids in order to investigate the solvent dependence of the reaction. Scheme 1 shows the formula of the complex and the studied substitution reaction.

The reaction follows the two-term rate law that is well known for substitution reactions at Pt(II) centres:[20]

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{nucleophile}] \quad (1)$$

in which $k_2$ refers to the bimolecular attack of the entering nucleophile displacing the coordinated chloride and $k_1$ to the solvolytic pathway which is generally small and much less precise. Under pseudo-first order kinetics equation 1 is simplified to:

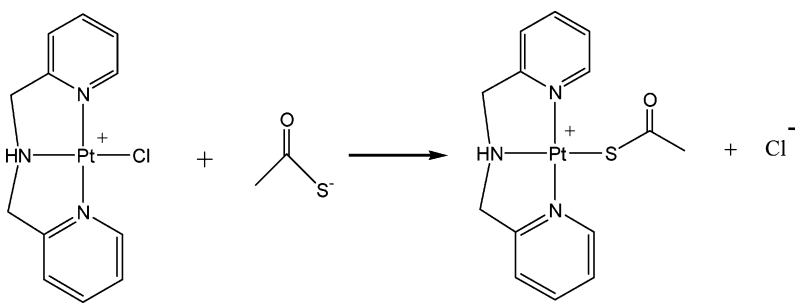
$$\text{rate} = k_{obs}[\text{complex}] \quad (2)$$

where $k_{obs}$ is defined as:

$$k_{obs} = k_1 + k_2[\text{nucleophile}] \quad (3)$$

and the second-order rate constant $k_2$ can be obtained by a linear fit of $k_{obs}$ *vs* [nucleophile].

The prepared complex is a cationic substrate with a tridentate chelate. The ligand was chosen due to its ability to interact strongly with the soft platinum(II) centre through π-bonding (accepting electron density from the $d_{xz}$ metal orbital), due to the presence of two aromatic nitrogen atoms, enhancing the electrophilicity and therefore reactivity of the complex.[16]




**Scheme 1**

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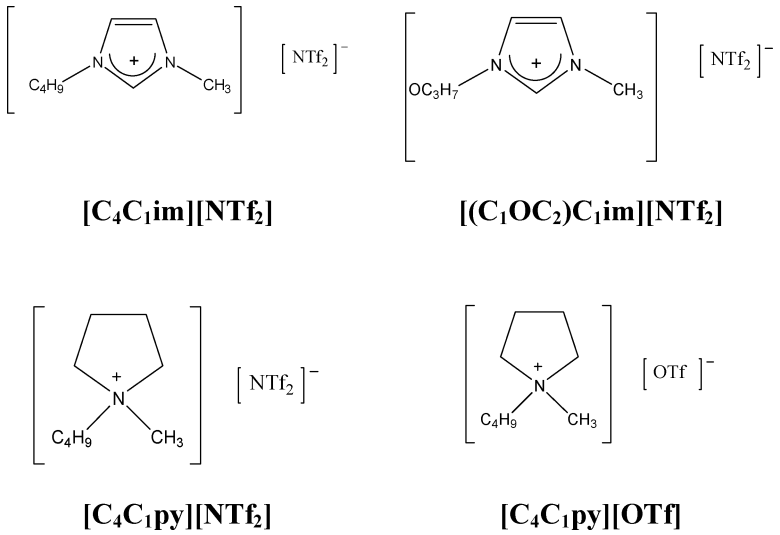


**[C$_4$C$_1$im][NTf$_2$]** **[(C$_1$OC$_2$)C$_1$im][NTf$_2$]**

**[C$_4$C$_1$py][NTf$_2$]** **[C$_4$C$_1$py][OTf]**

**Scheme 2**

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Although we tried to use ionic liquids with a wide variety of Kamlet–Taft polarity descriptors (see below), thioacetate was not soluble in [C$_4$C$_1$im][BF$_4$] and [C$_4$C$_1$im][OTf] and the complex was not soluble in [C$_4$C$_1$im][PF$_6$] {where [C$_4$C$_1$im] = 1-butyl-3-methylimidazolium}. In [C$_4$C$_1$im][MeSO$_4$] and [C$_4$C$_1$im][MePO$_4$] the reaction was reversible and the ionic liquid anions showed some nucleophilic character. Scheme 2 shows the ionic liquids in which the reactions were performed.

To the solutions of the complex in molecular solvents LiCl (0.002 M) was added to avoid solvolysis of the complex. Since we were studying the reaction between two charged reagents primary salt effects can influence the reaction and therefore all experiments were made at constant ionic strength. It was set to 0.01 M with LiClO$_4$ since higher concentrations of this salt in methanol caused precipitation in the nucleophile stock solution. The substitution reactions were studied by varying the concentration of the nucleophile and the temperature in all solvents. Table 1 contains the conditions used in the kinetic studies and the results obtained from the fitting (plots of $k_{obs}$ *vs* [SAc] are included in the ESI†). The second–order rate constants were corrected with the Debye–Hückel equation and the results reported in Table 2 are values extrapolated to zero-ionic strength ($k^{\circ}_2$).

The data clearly show that there is not a strong solvent dependency on $k_2$ when using thioacetate as the nucleophile, with only a 12-fold increase in rate on going from the slowest (MeOH) to the fastest solvent (H$_2$O). The reaction rate order obtained is MeOH < ionic liquids ≈ DMSO < H$_2$O, the ionic liquids behaving as polar aprotic solvents. If we consider the dielectric constant of the molecular solvents we can conclude that the reaction rate increases with increasing polarity of the solvent, since the order of polarity is: MeOH (32.66) < DMSO (46.45) < H$_2$O (80.16). The dielectric constants of some ionic liquids have been measured and shown to be in the range 10–15.[21] On the basis of our kinetic results one would have expected the values for the ionic liquids used here to be considerably higher. Nucleophilic substitutions have been used to investigate solvent effects on chemical reactions, and these have been rationalized as the Hughes–Ingold rules.[22–24] They predict that if charge is destroyed during the activation process (*e.g.*, as in associative substitution reactions of oppositely charged reagents), the effect of increased solvent polarity is to reduce the rate of reaction. Clearly, our data do not support this prediction and this failure might be due to the approach assuming an entirely electrostatic model of solvent–solute interactions and not taking into account the effect of specific interactions such as hydrogen bonding.

When analyzing solvent effects it is essential to consider the change in free energy of solvation of the central atom, which occurs during the activation process, in addition to the solvation of the entering group and of the coordinated ligands. The change in free energy of the coordinated metal when going from the starting complex to the more crowded 5-coordinate activated complex should depend on both steric and electronic factors.[25] Clearly, in our system several contributions are acting since we have used two protic and one dipolar aprotic solvent, and no reactivity pattern is observed concerning this solvent classification.

We can therefore conclude that there is a balance of opposing factors, which include H-bonding solvation, polarizability of the nucleophile and π interactions with the metal ion in the ground and in the activated state that determine the solvent effects, and which cannot be evaluated considering only the vague idea of solvent polarity, which is used in the Hughes–Ingold rules.

Van Eldik *et al.* studied the substitution reaction of the same complex (among other cationic substrates) with a neutral nucleophile, thiourea, and no correlation was found for solvent polarity and reaction rates, although with all substrates the reaction was faster in water than in MeOH, as in our system.[16]

### Kamlet–Taft LSER

A particularly successful approach when attempting to quantitatively understand solvent-dependent data is the linear solvation energy relationship (LSER). The equation, developed by Kamlet and Taft,[26–29] explains the variation of any solute property in terms of three microscopic properties ($\alpha$, $\beta$ and $\pi^*$). $\alpha$ is a quantitative scale of the hydrogen-bond acidity of a solvent, or its ability to donate a hydrogen bond; $\beta$ is a scale of the hydrogen-bond

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**Table 1** Concentrations used in the experiments and results from the pseudo-first order kinetics, $T = 25\ ^{\circ}C$

| Solvent | [Pt] × $10^4$ M | [KSAc] × $10^4$ M | $k_{obs}$ ($s^{-1}$) | $R^2$ | $k_2$ ($M^{-1}\ s^{-1}$) |
|---|---|---|---|---|---|
| MeOH | 0.900 | 21.6 | 0.00658 | | |
| | 0.895 | 32.2 | 0.00835 | | |
| | 0.891 | 42.7 | 0.0104 | | |
| | 0.903 | 56.3 | 0.0139 | | |
| | 0.900 | 64.7 | 0.0144 | | |
| | 1.07 | 85.5 | 0.0186 | | |
| | | | | 0.992 | 1.90 ± 0.09 |
| DMSO | 0.891 | 19.9 | 0.00145 | | |
| | 0.891 | 39.9 | 0.0265 | | |
| | 0.891 | 59.8 | 0.0380 | | |
| | 0.891 | 79.8 | 0.0482 | | |
| | 0.900 | 50.3 | 0.0337 | | |
| | | | | 0.995 | 5.7 ± 0.2 |
| $H_2O$ | 0.396 | 6.37 | 0.0120 | | |
| | 0.396 | 10.6 | 0.0259 | | |
| | 0.402 | 16.2 | 0.0413 | | |
| | 0.392 | 21.0 | 0.0568 | | |
| | 0.398 | 26.7 | 0.0789 | | |
| | | | | 0.996 | 32 ± 1 |
| $[C_4C_1im][NTf_2]$ | 0.900 | 9.63 | 0.00707 | | |
| | 0.891 | 19.1 | 0.0157 | | |
| | 0.900 | 28.9 | 0.0252 | | |
| | 0.891 | 38.1 | 0.0295 | | |
| | 0.900 | 48.2 | 0.0404 | | |
| | | | | 0.990 | 8.4 ± 0.5 |
| $[C_4C_1py][NTf_2]$ | 0.999 | 19.7 | 0.00630 | | |
| | 0.990 | 39.0 | 0.0141 | | |
| | 0.999 | 49.3 | 0.0206 | | |
| | 0.990 | 58.5 | 0.0237 | | |
| | 0.990 | 78.0 | 0.0332 | | |
| | | | | 0.996 | 4.6 ± 0.2 |
| $[C_4C_1py][OTf]$ | 1.10 | 10.3 | 0.00519 | | |
| | 1.09 | 20.4 | 0.0107 | | |
| | 1.10 | 30.9 | 0.0191 | | |
| | 1.09 | 40.7 | 0.0251 | | |
| | 1.10 | 51.4 | 0.0324 | | |
| | | | | 0.998 | 6.7 ± 0.2 |
| $[(C_1OC_2)C_1im][NTf_2]$ | 1.05 | 10.5 | 0.00925 | | |
| | 1.04 | 20.8 | 0.0189 | | |
| | 1.05 | 31.5 | 0.0283 | | |
| | 1.04 | 41.6 | 0.0378 | | |
| | 1.05 | 52.5 | 0.0470 | | |
| | | | | 0.999 | 9.00 ± 0.09 |

**Table 2** Kamlet–Taft parameters for the solvents used in this work. Second-order rate constants for the reaction $[Pt(dpma)Cl]^+ + SAc^- \rightarrow [Pt(dpma)SAc]^+ + Cl^-$ at 25 °C. Standard deviations included in brackets

| Solvent | $\alpha$ | $\beta$ | $\pi^*$ | $k^{\circ}_2$ ($M^{-1}\ s^{-1}$) |
|---|---|---|---|---|
| MeOH | 1.05 | 0.61 | 0.73 | 2.94 (0.09) |
| DMSO | 0.00 | 0.76 | 1.00 | 7.3 (0.2) |
| $H_2O$ | 1.17 | 0.47 | 1.09 | 36 (1) |
| $[C_4C_1im][NTf_2]$ | 0.62 | 0.24 | 0.98 | 8.4 (0.5) |
| $[C_4C_1py][NTf_2]$ | 0.43 | 0.25 | 0.95 | 4.6 (0.1) |
| $[C_4C_1py][OTf]$ | 0.4 | 0.46 | 1.02 | 6.7 (0.2) |
| $[(C_1OC_2)C_1im][NTf_2]$ | 0.63 | 0.23 | 0.99 | 9.00 (0.09) |

basicity of a solvent, or its ability to accept a hydrogen bond; and $\pi^*$ is the solvent dipolarity/polarizability, which is a scale of the ability of the solvent to stabilize a charge or dipole. Each of the parameters is empirically obtained and has been measured for a wide range of solvents, including ionic liquids.[11] These scales have been used in multi-parameter equations to fit a number of different solvent-dependent observations, with the most useful form shown in equation 4:

$$\ln k_2 = XYZ_0 + a\alpha + b\beta + s\pi^* \quad (4)$$

where $XYZ_o$, $a$, $b$ and $s$ are solvent-independent coefficients, characteristic of the process and an indicator of its sensitivity to the accompanying solvent property.

This methodology was applied to our data and the Kamlet–Taft parameters determined previously in our group for the ionic liquids used in this study[6,30,31] are reported in Table 2, along with ones from the literature.[11]

The error associated with each parameter of equation 3 was appraised in terms of the statistical $p$-value, and any terms found to be statistically insignificant were eliminated. It was decided to take as acceptable only those fittings where the statistical significance $p$-value for all coefficients did not exceed the limit level of 0.05. The results of these fits, along with the associated statistical data, are shown in Table 3 and graphically depicted in Fig. 1.

A very good correlation was obtained using equation 3 with data sets from both ionic liquids and all solvents. Hence, the data clearly demonstrate that, in this reaction at least, there is no special "ionic liquid effect" and that all significant interactions between

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**Table 3** Results of the Kamlet–Taft LSER fits for the reaction $[Pt(dpma)Cl]^+ + SAc^- \rightarrow [Pt(dpma)SAc]^+ + Cl^-$

| | LSER equation | *p*-values | $R^2$ |
|---|---|---|---|
| All data | $\ln k_2 = -4.8 + 1.1\alpha + 6.4\,\pi^*$ | $XYZ_0 = 0.010$<br>$a = 0.003$<br>$s = 0.021$ | 0.9182 |
| Only ILs | $\ln k_2 = -5.63 + 2.09\alpha + 6.58\,\pi^*$ | $XYZ_0 = 0.008$<br>$a = 0.005$<br>$s = 0.007$ | 0.9999 |

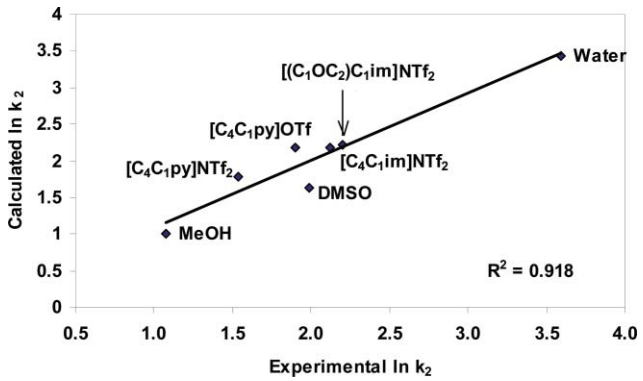


**Fig. 1** Kamlet–Taft LSER fit of $\ln k_2$.

the ionic liquids and these solutes are adequately described by an appropriate combination of their Kamlet–Taft parameters. Although a narrow range of $\pi^*$ values were used there is a correlation with a positive $\pi^*$ value, which is the opposite of the expected from the Hughes–Ingold interpretation. This suggests that $\pi^*$ is a poor indicator of Hughes–Ingold polarity. $\alpha$ is positive, meaning that an increase in the hydrogen-bond donating ability (acidity) of the solvent leads to an increase in the reaction rate.

Comparing the coefficients obtained for $\pi^*$ and $\alpha$, we can conclude that the polarizability of the solvent is the most important parameter in this system. MeOH, with the lowest polarizability, shows the lowest value for $k_2$. Solvation through van der Waals forces seems to stabilize the non-charged, highly polar transition state. The effect observed for H-bonding ability ($\alpha$) of the solvent is less important, since its coefficient is smaller. Solvents that are strong hydrogen bond donors accelerate the reaction. This effect becomes evident when comparing the pair $[C_4C_1py][NTf_2]/[C_4C_1im][NTf_2]$. For both ionic liquids the values of $\pi^*$ and $\beta$ barely differ but the higher value of $\alpha$ for $[C_4C_1im][NTf_2]$ leads to a significant increase (double) of the $k_2$ value. For ionic liquids this parameter is usually determined by the nature of the cation, but there is a smaller anion effect. Ionic liquids with imidazolium cations usually have high values due to the acidity of the aromatic protons.[31]

Hydrogen bond donor solvents can have a double action on the mechanism of substitution reactions: they can activate and facilitate the leaving of the chloride and enhance the reaction rate; on the other hand, there is the possibility to deactivate the nucleophile by hydrogen bonding with the electronegative atoms. Therefore the final effect of the hydrogen bond donating properties of the solvent will be given by the competition of these activating and deactivating processes. We are using a soft nucleophile, and the activation of the leaving group through stabilization via H-bonding donation from the solvent in the activated complex, seems to present a greater contribution to the changes in rate than the deactivation of the nucleophile.

**Table 4** Second order rate constants for the reaction of $[Pt(dpma)Cl]^+$ with thiourea,[16] dielectric constant (101.3 kPa) and Kamlet–Taft parameters for the solvents used[11]

| Solvent | $k_2$ ($M^{-1}s^{-1}$) | $\varepsilon$ (25 °C) | $\alpha$ | $\beta$ | $\pi^*$ |
|---|---|---|---|---|---|
| 1-propanol | 0.878 | 20.45 | 0.84 | 0.9 | 0.52 |
| Ethanol | 0.784 | 24.55 | 0.86 | 0.75 | 0.54 |
| Methanol | 0.588 | 32.66 | 1.05 | 0.61 | 0.73 |
| Water | 3.67 | 80.16 | 1.17 | 0.47 | 1.09 |

**Table 5** Results of the Kamlet–Taft LSER fits for the reaction $[Pt(dpma)Cl]^+ + TU \rightarrow [Pt(dpma)TU]^{2+} + Cl^-$

| LSER equation | *p*-values | $R^2$ |
|---|---|---|
| $\ln k_2 = 4.0 - 10.3\alpha + 8.5\,\pi^*$ | $XYZ_0 = 0.07$<br>$a = 0.03$<br>$s = 0.05$ | 0.998 |

Van Eldik *et al.* reported data on the reaction of $[Pt(dpma)Cl]^+$ with thiourea in several alcohols and water.[16] They were unable to find a direct correlation of the reaction rate and the solvent polarity or the Kamlet–Taft solvatochromic parameters. We decided to analyse their data with the Kamlet–Taft methodology. Table 4 contains the experimental data reported by them for this reaction along with the Kamlet–Taft descriptors for the solvents used in their study[11] and Table 5 contains the data from the correlation obtained with these solvent descriptors. The $R^2$ and the *p*-values show that the correlation is meaningful and once again the interactions are described by the polarity descriptors. For this type of reaction (one positively charged and one neutral reagent leading to charge delocalization over more atoms in the activated complex) once again the Hughes–Ingold rules predict a reduction of the rate of reaction with increasing solvent polarity, which is indeed observed for the alcohols, considering the dielectric constant (or the $\pi^*$ value) as a measure of the solvent polarity, however water clearly falls out of this prediction. There is a positive contribution from the dipolarity/polarizability of the solvent, which increases the reaction rate, as expected for a soft centre such as platinum(II), but now the reaction slows down with increasing H-bonding ability (acidity) of the solvent. Since the substrate is the same, the effect must be due to either the solvation of the nucleophile, which is soft, neutral and an H-bond donor and acceptor, or the activated complex, which is now positively charged, instead of polar non charged. Clearly both effects must be acting here.

### Eyring activation parameters

In order to gain an insight into the processes taking place the Eyring activation parameters were determined from the temperature studies ($20 < T < 40$ °C, 5 points, see ESI†). Table 6 presents the values obtained for the activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) in all the solvents, and Fig. 2 shows the correlation between both thermodynamic parameters.

The correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is very good ($r^2 = 0.975$) pointing to the same mechanism in all studied solvents. Changing the solvent from methanol (the slowest) to water (the fastest) leads

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**Table 6** Activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for the reaction of $[Pt(dpma)Cl]^+$ with thioacetate

| Solvent | $R^2$ | $\Delta H^{\ddagger}$ (kJ mol$^{-1}$) | $\Delta S^{\ddagger}$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| MeOH | 0.994 | 55 ± 3 | −98 ± 9 |
| DMSO | 0.998 | 49 ± 1 | −117 ± 4 |
| $H_2O$ | 0.989 | 39 ± 2 | −146 ± 8 |
| $[C_4C_1im][NTf_2]$ | 1.0 | 43.9 ± 0.3 | −129.7 ± 0.9 |
| $[C_4C_1py][NTf_2]$ | 0.992 | 50 ± 3 | −119 ± 9 |
| $[C_4C_1py][OTf]$ | 0.996 | 52 ± 4 | −107 ± 8 |
| $[(C_1OC_2)C_1im][NTf_2]$ | 0.999 | 44.9 ± 0.5 | −127 ± 2 |

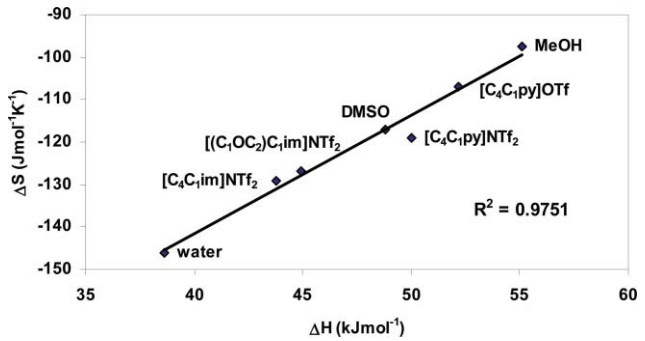


**Fig. 2** Plot of $\Delta S^{\ddagger}$ *vs.* $\Delta H^{\ddagger}$ for the substitution reaction of $[Pt(dpma)Cl]^+$ with thioacetate.

to a considerable decrease in the activation enthalpy and more negative entropies of activation. In the case of water the decrease in entropy can be associated with a higher number of structured molecules of solvent in the second coordination sphere of the transition state, in which hydrogen bonding plays a major role.[16] The same trend was observed in the reaction of $[Pt(dpma)Cl]^+$ with thiourea,[16] with $\Delta H^{\ddagger}$ values of 55 and 46 kJ mol$^{-1}$; and $\Delta S^{\ddagger}$ values of −65 and −81 J K$^{-1}$ mol$^{-1}$ for reactions conducted in methanol and water, respectively. The entropy decrease is considerably smaller in the case of thiourea, which is a weaker nucleophile than thioacetate, as shown by the lower $k_2$ values obtained (see Table 4). The less negative entropy is probably associated with the less structured transition state, as previously discussed.

While the molecular solvents show a broad range of values for $\Delta S^{\ddagger}$, ionic liquids show values that seem to depend on the cation. More negative values were obtained for the imidazolium cation containing ionic liquids, suggesting a more well-ordered structure in these solvents, in agreement with its higher ability to donate H-bonds through the acidic aromatic protons. The strongly negative values obtained for the entropy of activation (−98 to −146 J K$^{-1}$ mol$^{-1}$) are in agreement with the associative nature of the substitution reaction and an increase in the bond order in the transition state, as expected for square planar platinum(II) complexes.

## Conclusions

Although ionic liquids are considered green alternative solvents their effect on a reaction outcome cannot, at present, be predicted. The studied substitution reaction was selected as a test system for the effect of ionic liquids on a reaction mechanism. Although studies with other nucleophiles are necessary the results here suggest that ionic liquids are solvents with a range of different properties that can be described using the Kamlet–Taft approach; whereas the application of the Hughes–Ingold rules failed, in this particular substitution reaction, probably since they consider electrostatic forces only, ignoring specific interactions between solvent–solute, which are clearly important in this system. The application of the Kamlet–Taft approach in LSERs showed that there is no "ionic liquid effect", since the same correlation was obtained considering all solvents and ionic liquids only. It was observed that the effects for each solvent could not be extrapolated for other nucleophiles (like thiourea) since the nature of the nucleophile had effects on the reaction that could even alter the relative effects of the solvent.

The determined thermodynamic parameters indicated that the reaction mechanism is the same in all solvents and they are also in agreement with the associative nature of the substitution reaction, as expected for Pt(II).

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## References

1 (*a*) P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, VCH Wiley, Weinheim, 2002; (*b*) T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459–2477.
2 (*a*) V. I. Parvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615; (*b*) A. P. Abbott, G. Frisch and K. S. Ryder, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.*, 2008, **104**, 21–45; (*c*) P. J. Dyson, *Transition Met. Chem.*, 2002, **27**, 353.
3 BASF AG, 2008, Ch. WO 03/062171.
4 M. Freemantle, *Chem. Eng. News*, 2003, **81**, 9.
5 L. Crowhurst, N. L. Lancaster, J. M. P. Arlandis and T. Welton, *J. Am. Chem. Soc.*, 2004, **126**, 11549.
6 N. L. Lancaster, T. Welton and G. B. Young, *J. Chem. Soc. Perkin Trans.*, 2001, **2**, 2267.
7 N. L. Lancaster, P. A. Salter, T. Welton and G. B. Young, *J. Org. Chem.*, 2002, **67**, 8855.
8 N. L. Lancaster and T. Welton, *J. Org. Chem.*, 2004, **69**, 5986.
9 L. Crowhurst, R. Falcone, N. L. Lancaster, V. Llopis-Mestre and T. Welton, *J. Org. Chem.*, 2006, **71**, 8847.
10 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, 2003.
11 D. T. Richens, *Chem. Rev.*, 2005, **105**, 1961.
12 P. Illner, A. Zahl, R. Puchta, N. van Eikema Hommes, P. Wasserscheid and R. van Eldik, *J. Organomet. Chem.*, 2005, **690**(15), 3567–3576.
13 P. Illner, S. Kern, S. Begel and R. van Eldik, *Chem. Commun.*, 2007, 4803.
14 S. Begel, P. Illner, S. Kern, R. Puchta and R. van Eldik, *Inorg. Chem.*, 2008, **47**, 7121.
15 C. F. Weber, R. Puchta, N. J. R. V. Hommes, P. Wasserscheid and R. van Eldik, *Angew. Chem., Int. Ed.*, 2005, **44**, 6033.
16 C. F. Weber and R. van Eldik, *Eur. J. Inorg. Chem.*, 2005, **2005**, 4755.
17 L. Cammarata, S. G. Kazarian, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5192.
18 G. Hill, M. J. Irwin, C. J. Levy, L. M. Rendina and R. J. Puddephatt, *Inorg. Synth.*, 1998, **32**, 149.
19 *Tablecurve 2D AISN software*, Jandel Scientific.
20 F. Basolo and R. G. Pearson, *Mechanism of Inorganic reactions*, Wiley, New York, 1967.
21 H. Weingaertner, *Angew. Chem., Int. Ed.*, 2008, **47**, 654.
22 K. A. Cooper, M. L. Dhar, E. D. Hughes, C. K. Ingold, B. J. Macnulty and L. I. Woolf, *J. Chem. Soc.*, 1948, 2043.
23 E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1935, 244.

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24 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Bell, London, 1969.
25 U. Belluco, M. Graziani, M. Nicolini and P. Rigo, *Inorg. Chem.*, 1967, **6**, 721.
26 M. J. Kamlet, J. L. Abboud and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 6027.
27 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377.
28 R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 2886.
29 T. Yokoyama, R. W. Taft and M. J. Kamlet, J, *J. Am. Chem. Soc.*, 1976, **98**, 3233.
30 C. P. Fredlake, M. J. Muldoon, S. N. V. K. Aki, T. Welton and J. F. Brennecke, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3280.
31 L. Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790.

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