

RESEARCH ARTICLE

Tailoring the Surface Enrichment of a Pt Catalyst in Ionic Liquid Solutions by Choice of the Solvent

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The so-called buoy-effect, that is, the targeted surface enrichment of a Pt catalyst dissolved in ionic liquids (ILs), is achieved by attaching perfluorinated alkyl chains to the ligand system, which drags the metal complex toward the interface. Using angle-resolved X-ray photoelectron spectroscopy, it is demonstrated how this surface enrichment can be tailored by variation of the solvent IL. In $[C_nC_1Im][PF_6]$ ILs ($n = 2, 4, 8$), the surface is fully saturated with the complex at 10%_{mol} bulk content, while in $[C_4C_1Im][Tf_2N]$ only at 20%_{mol} saturation is observed. At low catalyst concentrations of 1%_{mol}, where saturation is not yet reached, the enrichment increases with decreasing length of the IL alkyl chain. As a general rule, the degree of surface enrichment decreases with the decrease in surface tension of the solvent IL, that is, in the order $[C_2C_1Im][PF_6] > [C_4C_1Im][PF_6] > [C_8C_1Im][PF_6] > [C_4C_1Im][Tf_2N]$. In ILs with very low surface tension, enrichment is even suppressed. These results reveal the surface tension of the solvent IL as rational parameter for tailoring the interfacial structure of IL-based catalyst systems, such as supported ionic liquid phase (SILP) catalysis, where the nature of the IL/gas interface is expected to strongly influence the performance of the process.

in order to facilitate both more ecological and economical chemical processes.^[1] Commercial-scale catalysis is governed by heterogeneous systems promising, for example, robustness, facile product separation and low catalyst loss. A common challenge with technical heterogeneous catalysts, however, is the oftentimes poor selectivity and low atom utilization,^[2] which is undesired in light of the growing demand for more sustainable processes. In addition to interesting advances toward boosting the selectivity of heterogeneous catalysts in the recent past,^[2,3] also homogeneous organometallic complexes have become increasingly attractive, as they provide well-defined catalytic centers with uniform reactivity and thus high selectivity. Nonetheless, the attractiveness of these homogeneous catalysts for industry is still widely limited, due to challenging separation protocols and their sensitivity to harsh reaction

1. Introduction

Design, characterization, and optimization of innovative catalytic systems play a central role in modern science and engineering,

conditions. Therefore, significant efforts have been dedicated to the design of novel hybrid systems for immobilization of homogeneous catalysts on solid supports, which aim to merge the benefits of homogeneous and heterogeneous catalysis.^[4]

Supported Ionic Liquid Phase (SILP) catalysis has emerged as a particularly promising immobilization technique.^[5] SILP systems are hybrid materials featuring a thin liquid film of a homogeneous catalyst dissolved in an ionic liquid (IL), which is adsorbed onto a large-surface-area support.^[5b,c] The actual catalyst maintains its homogeneous character in the liquid phase, while the macroscopically solid SILP material can be employed just like a heterogeneous catalyst. The choice of ILs as the liquid solvent phase has several benefits: Being liquid salts, ILs show an extremely low vapor pressure and a high thermal stability; thus, they provide durable films suitable for rougher reaction conditions and continuous flow applications.^[6] The ionic character of ILs also yields a different spectrum of solvent–solute interactions as compared to conventional molecular solvents, which can indeed be beneficial for the reaction outcome, as has been shown for a variety of catalyzed transformations.^[7] Additionally, due to their widely organic composition, the chemical structure of ILs can be tailored toward task-specific properties, for example, regarding solvation and miscibility of/with reactants and products, stabilization of intermediates and transition states, viscosity, and interfacial tension.

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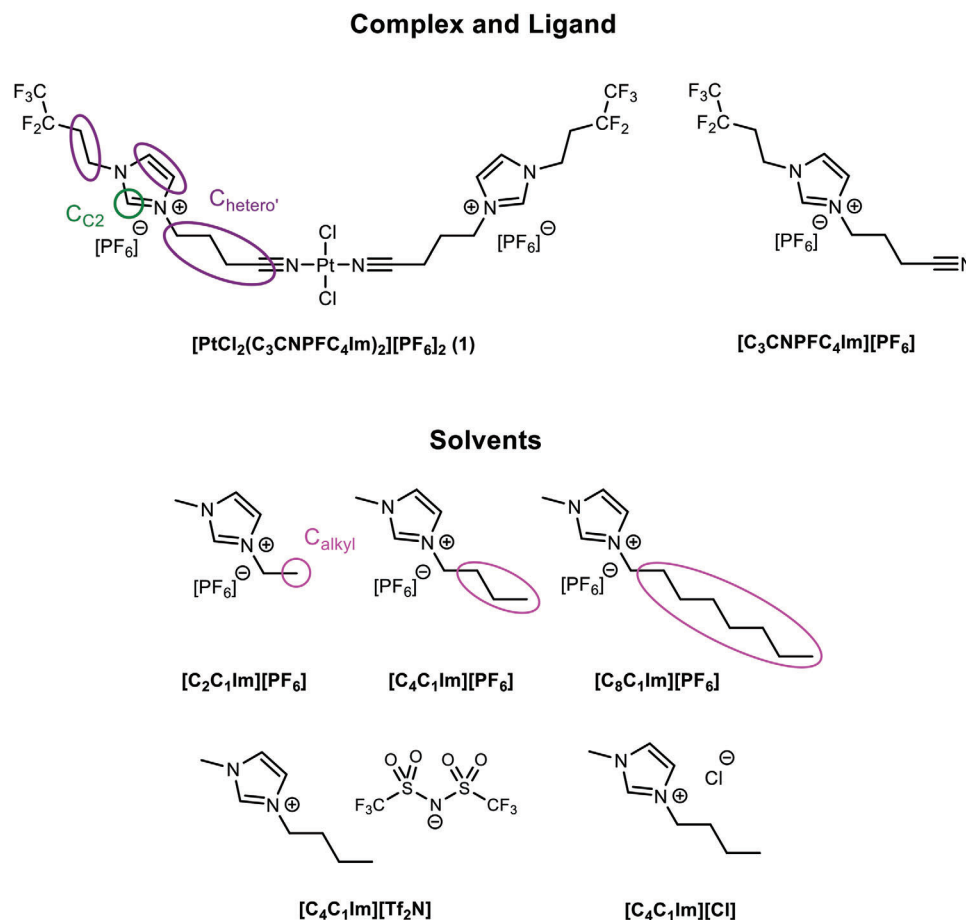


Figure 1. Molecular structures of materials employed in this work: Complex and ligand: $[\text{PtCl}_2(\text{C}_3\text{CNPF}_4\text{Im})_2][\text{PF}_6]_2$ (1) (top left), $[\text{C}_3\text{CNPF}_4\text{Im}][\text{PF}_6]$ (top right), Solvent ILs: $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$ (middle left), $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$ (center), $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$ (middle right), $[\text{C}_4\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ (bottom left) and $[\text{C}_4\text{C}_1\text{Im}][\text{Cl}]$ (bottom right). Color coding indicates assignment of carbon species detected in XPS.

The large contact area of SILP catalysts with the surrounding reactant/product phase renders a fundamental understanding on the interfacial structures inevitable for most efficient application.^[8] In fact, the nature of the IL/gas or vacuum interface of ILs was explored with a wide variety of well-established surface science techniques, targeting surface composition, enrichment effects, and preferential orientation and layering of ions and functional groups at the interface.^[9] In particular, X-ray photoelectron spectroscopy (XPS) has been employed intensively in this regard by various groups, including ours.^[8,9b,f,10] The power of this technique is that it enables quantitative insights into the elemental composition of the near-surface region along with chemical/electronic information of the atoms probed. The knowledge of these attributes has also shown to be highly beneficial in the study of IL solutions of organometallic catalysts and metal salts.^[10h,11] The surface sensitivity of this technique can be tuned by varying the emission angle of the photoelectrons, which is referred to as angle-resolved XPS (ARXPS) and allows for an even more detailed structural picture on the IL/vacuum interface of catalyst systems.^[10h,11a-c,k,12]

Using ARXPS, we recently demonstrated the manipulation of the surface concentration of a Pt complex in $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$ by attaching perfluorinated alkyl chains to the ligand system.^[11a,k]

These substituents induce a strong enrichment of the catalyst at the IL/vacuum interface in a buoy-like fashion pulling the molecule toward the surface.^[11a] The driving force for the pronounced surface accumulation of the catalyst is the lowering in surface free energy, as was deduced from the surface tension measured using the pendant drop (PD) method.^[11k] Our study showed that the magnitude of this so-called buoy effect can be controlled via several parameters: a) Catalyst concentration: The surface enrichment was found most pronounced at lowest concentration promising high atom utilization in catalytic applications;^[11a,k] b) temperature: The surface concentration of the catalyst increases with decreasing temperature making this concept particularly interesting for low-temperature catalysis;^[11k] c) the number of surface-active ligands attached to the metal center.^[11k]

The intention of this study is to evaluate another important parameter for tailoring the surface enrichment and structure of such catalytic systems, that is, the variation of the IL solvent. For this purpose, we investigated solutions of the previously employed Pt catalyst (1) in a variety of ILs using ARXPS. The structure of 1 and of the IL solvents are depicted in Figure 1. As reported previously, 1 was directly synthesized in $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$.^[11a,k] Herein, we successfully expanded

this preparation procedure to $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$, $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$, and $[\text{C}_4\text{C}_1\text{Im}][\text{TF}_2\text{N}]$; notably, in $[\text{C}_4\text{C}_1\text{Im}][\text{Cl}]$, formation of **1** was not successful, which we attribute to coordination of the excess Cl^- anions. The $[\text{PF}_6]^-$ -based ILs only differ in the chain length of the alkyl substituent on the $[\text{C}_n\text{C}_1\text{Im}]^+$ cation. For a variety of pure imidazolium-based ILs, the alkyl chain length was shown to have decisive influence on the structure of the IL/gas or vacuum interface: longer alkyl chains (number of carbon atoms (n) ≥ 4) preferably terminate the surface, while short alkyl chains ($n < 4$) show no or a much lower surface activity.^[9b,d,i,j,l,13] From our ARXP spectra of neat $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$ at room temperature, we are able to show that this behavior also holds for the series of $[\text{PF}_6]^-$ ILs. By also employing $[\text{C}_4\text{C}_1\text{Im}][\text{TF}_2\text{N}]$ as the solvent, we provide additional information on the influence of the IL anion on the surface enrichment of **1**. For all solutions, we found **1** to be strongly surface-enriched, with saturation occurring at sufficiently high catalyst concentrations. At 1%_{mol}, where the surface is not saturated yet, the enrichment of **1** follows the trend of the surface tension of the ILs ($[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6] > [\text{C}_4\text{C}_1\text{Im}][\text{PF}_6] > [\text{C}_8\text{C}_1\text{Im}][\text{PF}_6] > [\text{C}_4\text{C}_1\text{Im}][\text{TF}_2\text{N}]$). This behavior demonstrates that the surface concentration of the catalyst is strongly influenced by the surface free energy of the solvent. For $[\text{C}_4\text{C}_1\text{Im}][\text{Cl}]$, where the preparation of **1** was not successful, we studied solutions of only the ligand $[\text{C}_3\text{CNPF}_4\text{Im}][\text{PF}_6]$ (see Figure 1) in $[\text{C}_4\text{C}_1\text{Im}][\text{Cl}]$ and $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$, and find the same influence of the solvent's surface tension on the surface enrichment of the ligand. For all neat ILs, the surface tensions were determined in our recently developed chamber ensuring ultraclean vacuum conditions.^[14]

2. Results and Discussion

2.1. Expanding the Synthesis of **1** to Several IL Solvents

We recently reported the successful formation of **1** in $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$ using XPS on solutions with sufficiently high concentrations to clearly elucidate the stoichiometry of the complex.^[11a,k] Herein, we expand this approach to solutions of **1** in $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$, $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$, and also $[\text{C}_4\text{C}_1\text{Im}][\text{TF}_2\text{N}]$. In Figure 2a–e, the Pt 4f, F 1s, N 1s, and C 1s spectra of the concentrated solutions of **1** in $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$, $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$, $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$, and $[\text{C}_4\text{C}_1\text{Im}][\text{TF}_2\text{N}]$ are plotted on top of each other, in 0° (black, more bulk-sensitive) and 80° emission (red, more surface-sensitive); full sets of spectra are shown in Figures S2–S6 (Supporting Information). The quantitative analyses of binding energies and signal intensities are provided in Table 1a–e. For all solutions, the Pt 4f_{7/2} signals were detected at 74.2 eV $\pm$ 0.2 eV, indicating the same ligand environment of the metal center. All other signals also nicely agree with the binding energies expected from previous works on **1**^[11a] or similar complexes,^[11c] and with those of the $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$, $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$, and $[\text{C}_4\text{C}_1\text{Im}][\text{TF}_2\text{N}]$ from literature.^[10a,b,15] Since to the best of our knowledge no detailed ARXPS data of $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$ at room temperature was published yet, the corresponding spectra and the quantitative analysis are shown in Figure S1 and Table S1 (Supporting Information). As is evident from Table 1a–e, the detected intensities of the complex-specific signals, that is, Pt 4f, Cl 2p and $\text{N}_{\text{CNcoord}}$, match the expected stoichiometry (1:2:2 ratio of these signals) of **1**. This

agreement confirms the chemical state and stoichiometry of the studied systems since non-volatile degradation products of the synthesis should be visible in the XP spectra. Note that due to the strong surface affinity of the fluorinated side chains in the ligand system, even at 0° (more bulk-sensitive) the F_{CFx} signal in the solutions of the $[\text{PF}_6]^-$ ILs always shows a larger intensity than expected, that is, a $\text{F}_{\text{CFx}}:\text{Pt}$ ratio of $\approx 14:1$ instead of the nominal ratio of 10:1.^[11a,k] Overall, these results confirm successful formation of **1** also in $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$, $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$, and $[\text{C}_4\text{C}_1\text{Im}][\text{TF}_2\text{N}]$.

To get more detailed insights into the influence of the anion on the enrichment of **1**, we also attempted synthesis of the catalyst in another $[\text{C}_4\text{C}_1\text{Im}]^+$ -IL, that is, $[\text{C}_4\text{C}_1\text{Im}][\text{Cl}]$. However, this synthesis was not successful, most probably due to the coordinating behavior of the excess Cl^- anions, as is described in detail in the supporting information (see Figure S8 and Table S3 and text, Supporting Information). Since no detailed ARXPS investigation of neat $[\text{C}_4\text{C}_1\text{Im}][\text{Cl}]$ at room temperature was published yet, we also show the corresponding spectra (see Figure S7 and Table S2, Supporting Information).

2.2. Surface Composition of Concentrated Solutions of **1**

Next, we discuss the surface composition of the concentrated solutions of **1** in $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$, $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$ and $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$, and $[\text{C}_4\text{C}_1\text{Im}][\text{TF}_2\text{N}]$ by means of the ARXP spectra shown in Figure 2a–e (the spectra for **1** in $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$ have been adapted from Ref. [11a,k]). Overall, the $[\text{PF}_6]^-$ -based IL solutions in Figure 2a–c shows very similar intensities in 0° and also in 80° emission. This is particularly true for the complex-specific Pt 4f, F_{CFx} , $\text{N}_{\text{CNcoord}}$, C_{CF3} , and C_{CF2} signals, and for the Cl 2p signal, as is also evident from Table 1a–c and Figures S2–S4 (Supporting Information). Inspection of Table 1a–c reveals that at 80° the complex-specific signals are strongly enhanced as compared to the nominal composition, which indicates that **1** is strongly enriched at the surface. The nearly identical spectra for the three solutions in 80° emission confirm a similar composition at the surface for the three solutions, namely, saturation with **1**, as concluded from previous works on solutions of **1** in $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$.^[11a,k] Notably, we observe an enhancement also for 0° emission, which is a common observation in case of very strong surface enrichment of a species in IL mixtures and IL solutions.^[11a,k] Moreover, if we compare the 80° and 0° spectra, we find more or less no increase for the Pt 4f signals, but a pronounced increase of the F_{CFx} signals. From this observation, we can deduce the orientation of **1** at the surface, with the surface-active fluorinated side chains of the ligand system pointing toward the vacuum and the Pt center toward the bulk. This orientation leads to a relative attenuation of the corresponding Pt signal at 80°, yielding a similar intensity as at 0°. [11a] The small differences in the 0° spectra for the F_{PF6} , N_{Im} , C_2 and C_{hetero} signals, which stem from both **1** and the ILs, are due the different bulk densities of the solutions (see Table 4). As expected, the IL-specific C_{alkyl} signal at 0° increases with increasing alkyl chain length of the $[\text{C}_n\text{C}_1\text{Im}]^+$ cation. Notably, at 80° for all solutions, the C_{alkyl} signal drastically decreases, so that for the solution of $[\text{C}_2\text{C}_1\text{Im}][\text{PF}_6]$ no appropriate fitting could be achieved, while for $[\text{C}_4\text{C}_1\text{Im}][\text{PF}_6]$ and $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$ low-intensity signals could be

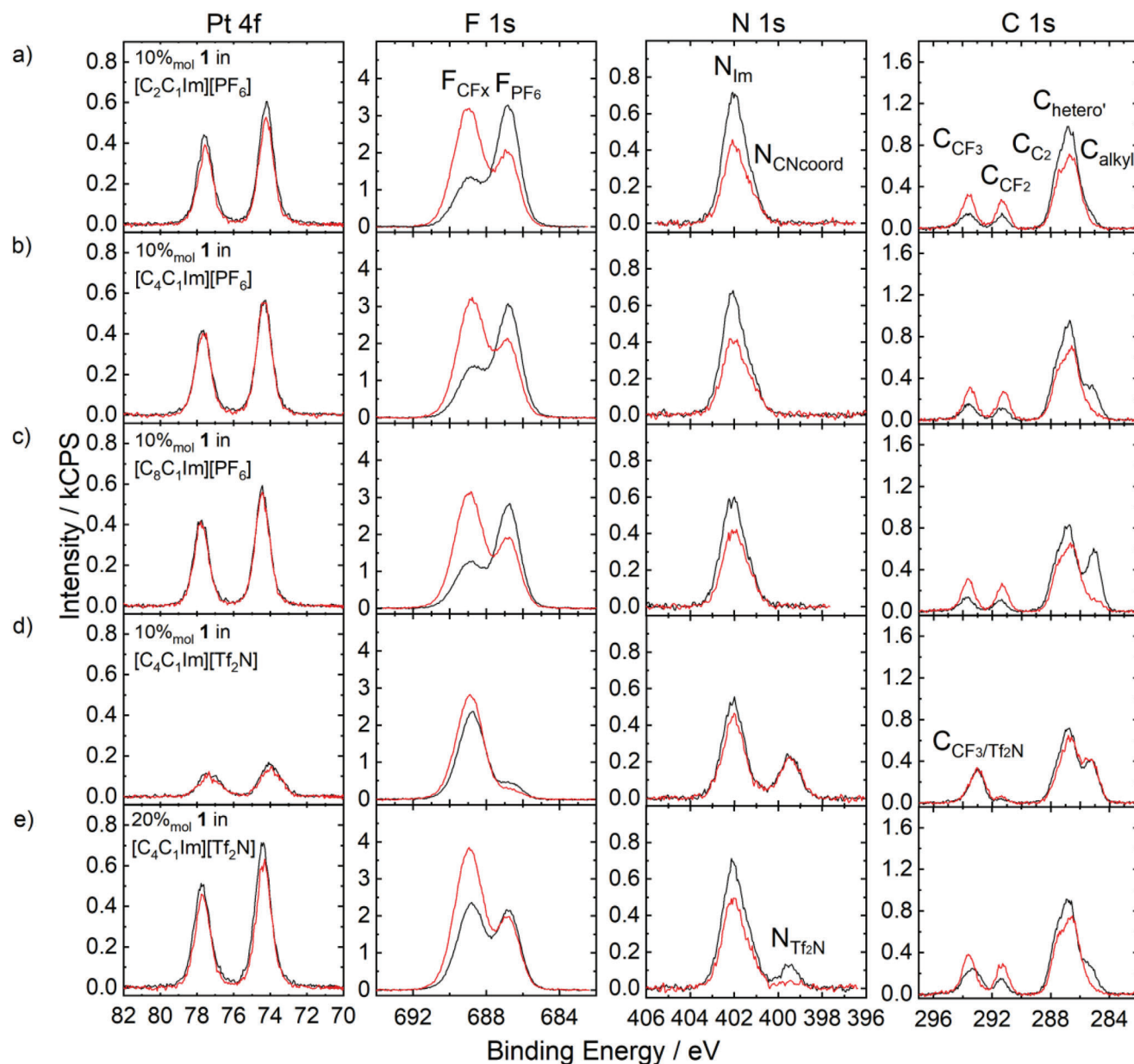


Figure 2. Pt 4f (left), F 1s (middle left), N 1s (middle right) and C 1s (right) XP spectra of 10%_{mol} solutions of **1** in a) [C₂C₁Im][PF₆], b) [C₄C₁Im][PF₆], c) [C₈C₁Im][PF₆] and d) [C₄C₁Im][Tf₂N], as well as e) a 20%_{mol} solution of **1** in [C₄C₁Im][Tf₂N] in 0° (black) and 80° emission (red). For assignment of signals to the molecular structures see Figure 1. All spectra were recorded at room temperature.

deconvolved. This decrease is assigned to the depletion of the solvent IL from the surface layer caused by the enrichment of **1**.

The 10%_{mol} solution of **1** in [C₄C₁Im][Tf₂N] depicted in Figure 2d displays a quite different behavior than the equimolar [PF₆][−] solutions discussed above. The intensity of the complex-specific Pt 4f, N_{CNcoord}, and C_{CF2} signals is much lower and, in fact, excellently corresponds to the nominal composition of the solution, as is evident from Table 1d. All other signals also nicely match the nominal values, suggesting a homogeneous distribution of the complex at the IL/vacuum interface and in the bulk at 10%_{mol} catalyst loading. Note that the F_{CFx} and C_{CF3} signals contain contributions from both **1** and the [Tf₂N][−] anion. The rela-

tively broad C_{CF3/Tf2N} signal is attributed to the fact that the carbon atoms of the CF₃ groups in **1** and [Tf₂N][−] are chemically not equal due to different binding partners, that is, carbon (−CF₂) in **1** and sulfur (−SO₂) in [Tf₂N][−]. At 80°, the F_{CFx} signal shows an increase of ≈20%, while all other signals remain constant or show a slight decline. This behavior results from the preferential surface orientations of the complex^[11a] and the [Tf₂N][−] anion, both of which direct their CF_x groups toward the IL/gas or vacuum interface. Such an orientation is well established, also for other IL anions containing terminal perfluorinated carbon groups.^[8,10c,11b,13,15,16]

Increasing the catalyst concentration in [C₄C₁Im][Tf₂N] from 10%_{mol} to 20%_{mol} results in a disproportional increase of the

Table 1. Quantitative analysis of XPS core level spectra of 10%_{mol} solutions of [PtCl₂(C₃NPFC₄Im)](PF₆)₂ (1) in a) [C₂C₁Im](PF₆), c) [C₈C₁Im](PF₆), d) [C₄C₁Im](PF₆), and with e) 20%_{mol} catalyst concentration in [C₄C₁Im](PF₆)₂ N]. “Nominal” indicates the relative numbers of the atoms derived from the nominal stoichiometry, and “Experimental” the corresponding numbers deduced from the XPS data at 0° and 80°. *For the spin-orbit-split signals, the indicated binding energy values correspond to larger peak, that is, Pt 4f_{7/2}, Pt 2p_{3/2}, P 2p_{3/2}, and S 2p_{3/2}.

	Pt 4f*	Cl 2p*	F 1s CFx	F 1s PF ₆	N 1s Im	N 1s CNcoord	N 1s Tf ₂ N	C 1s CF ₃	C 1s CF ₂	C 1s C ₂	C 1s hetero'	C 1s alkyl	P 2p*	O 1s	S 2p*
a) 10%_{mol} 1 in [C₂C₁Im](PF₆)															
Binding Energy / eV	74.2	199.0	688.9	686.8	402.1	401.3		293.6	291.3	287.6	286.7	285.3	136.6		
Nominal	0.11	0.22	1.1	7.3	2.4	0.22		0.22	0.22	1.2	5.8	1.0	1.2		
Experimental, 0°	0.22	0.44	3.1	5.7	1.9	0.46		0.61	0.61	0.97	5.6	0.33	1.1		
Experimental, 80°	0.19	0.38	7.3	3.4	1.2	0.37		1.2	1.2	0.58	4.5		0.75		
b) 10%_{mol} 1 in [C₄C₁Im](PF₆) [1 Ta, k]															
Binding Energy / eV	74.3	199.0	688.7	686.8	402.1	401.2		293.6	291.3	287.7	286.8	285.1	136.8		
Nominal	0.11	0.22	1.1	7.3	2.4	0.22		0.22	0.22	1.2	5.8	3.0	1.2		
Experimental, 0°	0.23	0.50	3.3	5.9	2.0	0.53		0.66	0.66	1.0	5.8	1.3	1.1		
Experimental, 80°	0.23	0.44	7.8	3.8	1.3	0.42		1.3	1.3	0.64	4.9	0.13	0.86		
c) 10%_{mol} 1 in [C₈C₁Im](PF₆)															
Binding Energy / eV	74.4	199.1	688.9	686.8	402.1	401.4		293.8	291.5	287.7	286.8	285.1	136.9		
Nominal	0.11	0.22	1.1	7.3	2.4	0.22		0.22	0.22	1.2	5.8	7.0	1.2		
Experimental, 0°	0.28	0.55	3.9	6.5	2.2	0.54		0.69	0.69	1.1	6.2	3.2	1.2		
Experimental, 80°	0.26	0.49	9.5	4.2	1.4	0.54		1.5	1.5	0.70	5.7	0.35	0.91		
d) 10%_{mol} 1 in [C₄C₁Im](PF₆)₂ N]															
Binding Energy / eV	74.0	198.9	688.8	686.6	402.1	401.2	399.5	293.1	291.3	287.7	286.8	285.2	136.7	532.7	169.1
Nominal	0.11	0.22	7.1	1.3	2.4	0.22	1.0	2.2	0.22	1.2	5.8	3.0	0.22	4.0	2.0
Experimental, 0°	0.12	0.23	7.6	1.0	2.5	0.19	1.0	2.3	0.18	1.2	5.7	2.7	0.22	4.0	2.0
Experimental, 80°	0.11	0.18	9.3	0.6	2.1	0.14	1.0	2.6	0.25	1.0	5.1	2.9	0.17	3.7	2.0
e) 20%_{mol} 1 in [C₄C₁Im](PF₆)₂ N]															
Binding Energy / eV	74.4	199.1	688.8	686.8	402.1	401.3	399.5	293.4	291.4	287.7	286.8	285.2	136.8	532.7	169.1
Nominal	0.25	0.50	8.5	3.0	3.0	0.50	1.0	2.5	0.50	1.5	8.0	3.0	0.50	4.0	2.0
Experimental, 0°	0.44	0.88	8.3	5.9	3.1	0.80	0.53	2.4	0.83	1.5	8.7	1.4	0.95	2.0	1.1
Experimental, 80°	0.37	0.75	13.9	5.2	2.2	0.62	0.19	2.8	1.9	1.1	7.9	0	1.1	0.50	0.30

complex-specific Pt 4f, F_{CFx} , F_{PF_6} , and $N_{CNcoord}$ signals in 0° and 80° (e.g., for Pt by a factor of ≈ 3.5 in 0°, instead of the expected factor of ≈ 2), as evident from the comparison of Figure 2d,e. Accordingly, the intensities of all complex-specific signals in Table 1e are much higher than expected from the nominal composition, while signals stemming from **1** and IL (N_{Im} , C_2 , and $C_{hetero'}$) agree with the nominal values, and the IL-specific signals (N_{TF_2N} , C_{alkyl} , O 1s, S 2p) are much smaller than the nominal values 0° and 80°. These findings are in line with a strong enrichment of the complex at the IL/vacuum interface, similar to that observed for the surface-saturated $[PF_6]^-$ solutions. The very similar Pt 4f intensity at 80° for the $[TF_2N]^-$ and the $[PF_6]^-$ solutions (compare Figure 2e vs Figure 2a–c) indicates that at 20%_{mol} the $[TF_2N]^-$ solution the surface is also saturated with the complex. The surface enrichment of the complex in the 20%_{mol} solution is also evident from the strong increase of the F_{CFx} signal at 80° as compared to 0° (see Figure 2e); notably for the homogeneous 10%_{mol} solution in $[C_4C_1Im][TF_2N]$ only small increase is observed (see Figure 2d). Overall, these results indicate that inducing surface enrichment of **1** in $[C_4C_1Im][TF_2N]$ requires a higher concentration of the catalyst than for the $[PF_6]^-$ ILs. This observation is assigned to the particularly low surface tension of $[C_4C_1Im][TF_2N]$ as will be discussed in more detail later. Due to its lower surface tension, $[C_4C_1Im][TF_2N]$ exhibits a higher driving force toward the surface than the $[PF_6]^-$ ILs, so that a higher concentration of surface-active catalyst is required to significantly lower the surface free energy by its accumulation at the interface.

For the 20%_{mol} solution of **1** in $[C_4C_1Im][TF_2N]$, it is also interesting to discuss the surface behavior of the anions in more detail, since for this system solvent and solute have different anions, that is, $[TF_2N]^-$ and $[PF_6]^-$. Several groups have dedicated significant interest in related IL mixtures with these anions in the recent past.^[17] In Figure 2d, the F_{PF_6} signal, which is only due to the ionic complex **1**, shows a much higher intensity at both 0° and 80° than expected from the nominal composition. At the same time, the N_{TF_2N} signal, which is only due to the solvent IL, shows a much lower than nominal intensity at 0° and was barely detected at 80°. This behavior reveals that the $[PF_6]^-$ anion is enriched at the IL/vacuum interface, along with its original metal-containing counter ion. This finding is quite surprising since the $[TF_2N]^-$ anion typically is enriched in binary mixtures of $[TF_2N]^-$ and $[PF_6]^-$ ILs^[17], but also in mixtures with ILs containing other anions.^[9g,10f,i] The reason for the enrichment of the $[PF_6]^-$ anion could be a more efficient packing in the closed layer of **1** at the IL/vacuum interface with the smaller $[PF_6]^-$ anion rather than the larger $[TF_2N]^-$.

2.3. Surface Composition of 1%_{mol} Solutions of **1**

After discussing the concentrated solutions, we next address ARXP spectra of more diluted solutions with 1%_{mol} of **1** dissolved in the ILs, that is, a concentration regime, where we do not expect the IL/vacuum interface to be fully saturated with **1**, as was shown for a solution of $[C_4C_1Im][PF_6]$ in a previous study.^[11k] Figure 3 shows the Pt 4f, F 1s, and C 1s spectra of the 1%_{mol} solutions of **1** in $[C_2C_1Im][PF_6]$ (black), $[C_4C_1Im][PF_6]$ (green) and $[C_8C_1Im][PF_6]$ (blue), at 0° (left) and 80° (right). For comparison, also the Pt 4f signals of a 1%_{mol} solution of **1** in $[C_4C_1Im][TF_2N]$

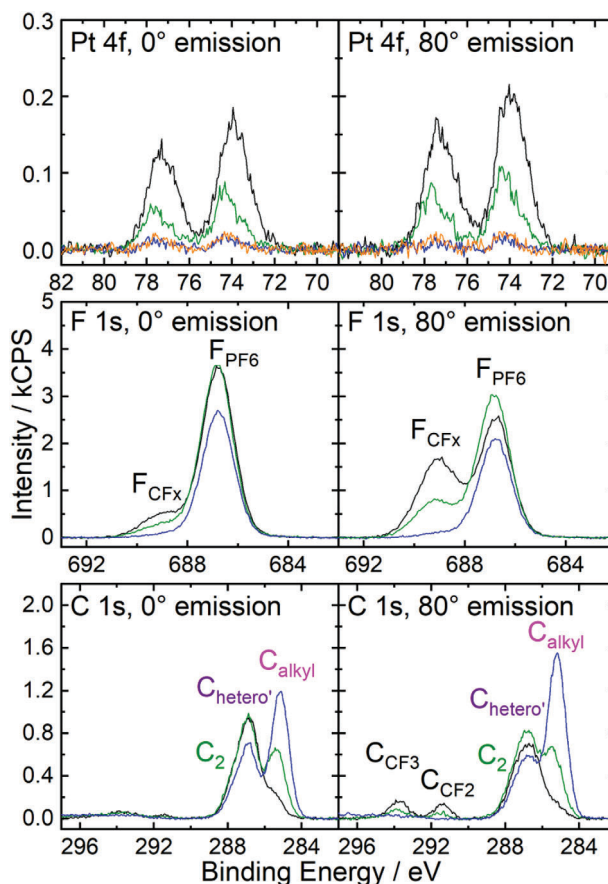


Figure 3. Pt 4f (top), F 1s (middle), and C 1s (bottom) XP spectra of 1%_{mol} solutions of **1** in $[C_2C_1Im][PF_6]$ (black), $[C_4C_1Im][PF_6]$ (green) and $[C_8C_1Im][PF_6]$ (blue) in 0° (left) and 80° emission (right). In addition, Pt 4f spectra of a 1%_{mol} solution of **1** in $[C_4C_1Im][TF_2N]$ (orange) are shown. For assignment of signals to the molecular structures see Figure 1. All spectra were recorded at room temperature.

(orange) are depicted. Full sets of ARXP spectra of these solutions are depicted in Figures S9–S12 (Supporting Information), and the quantitative analysis is provided in Table 2a–d.

As evident from Figure 3, the complex-related Pt 4f and F_{CFx} signals at 0° and 80° strongly increase in intensity with decreasing chain length on the $[C_nC_1Im]^+$ cation, that is, they are smallest for the $[C_8C_1Im][PF_6]$ and largest for the $[C_2C_1Im][PF_6]$ solution. This finding reveals that the enrichment of **1** at the IL/vacuum interface is more pronounced for short alkyl substituents on the $[C_nC_1Im]^+$ cation. For the $[C_8C_1Im][PF_6]$ solution, the Pt 4f intensity is actually in line with the nominal composition of the solution indicating homogeneous distribution of **1** at the surface and in the bulk. Hence, the surface activity of **1** can even be suppressed at 1%_{mol} due to competition with the surface-affine octyl chain of the solvent, as will be discussed further below.

The opposite trend is found for the IL-specific C_{alkyl} signals in Figure 3, which show an increase upon increasing the chain length on the imidazolium cation. The magnitude of the increase is stronger than expected from the nominal increase (1, 3, and 7 C_{alkyl} atoms in the different ILs, see Figure 1), which is attributed

Table 2. Quantitative analysis of XPS core level spectra of 1%_{mol} solutions of **1** in a) [C₂C₁Im][PF₆], b) [C₄C₁Im][PF₆], c) [C₆C₁Im][PF₆], and d) [C₈C₁Im][Tf₂N]. "Nominal" indicates the relative numbers of the atoms derived from the nominal stoichiometry, and "Experimental" the corresponding numbers deduced from the XPS data at 0° and 80°. For the spin-orbit-split signals, the indicated binding energy values correspond to larger peak, that is, Pt 4f_{7/2}, Cl 2p_{3/2}, P 2p_{3/2}, and S 2p_{3/2}.

a) 1% _{mol} 1 in [C ₂ C ₁ Im][PF ₆]	Pt 4f [*]	Cl 2p [*]	F 1s CFx	F 1s PF ₆	N 1s Im	N 1s CNcoord	N 1s Tf ₂ N	C 1s CF ₃	C 1s CF ₂	C 1s C ₂	C 1s hetero [*]	C 1s alkyl	P 2p [*]	O 1s	S 2p [*]
Binding Energy / eV	73.9	199.1	688.9	686.8	402.1	401.2	293.8 (80°)	291.5 (80°)	287.7	286.8	285.4	136.8			
Nominal	0.010	0.020	0.10	6.1	2.0	0.020	0.020	0.020	1.0	4.2	1.0	1.0			
Experimental, 0°	0.089	0.16	1.1	5.6	1.8	0.11			0.92	4.0	0.73	1.0			
Experimental, 80°	0.11	0.19	3.3	3.9	1.3	0.11	0.60	0.60	0.65	3.7	0.27	0.76			
b) 1% _{mol} 1 in [C ₄ C ₁ Im][PF ₆] ^[11k]															
Binding Energy / eV	74.2	199.1	688.8	686.8	402.2		293.9 (80°)	291.6 (80°)	287.8	286.9	285.4	136.9			
Nominal	0.010	0.020	0.10	6.1	2.0	0.020	0.020	0.020	1.0	4.2	3.0	1.0			
Experimental, 0°	0.037	0.074	0.77	5.9	2.0				1.0	4.0	2.7	1.1			
Experimental, 80°	0.051	0.090	1.7	5.0	1.7		0.29	0.29	0.85	4.0	2.6	0.98			
c) 1% _{mol} 1 in [C ₆ C ₁ Im][PF ₆]															
Binding Energy / eV	74.2	198.9	688.9	686.8	402.2				287.8	286.9	285.2	136.8			
Nominal	0.010	0.020	0.10	6.1	2.0	0.020	0.020	0.020	1.0	4.2	7.0	1.0			
Experimental, 0°	0.011	0.029	0.27	6.1	2.0				1.0	4.1	6.8	1.1			
Experimental, 80°	0.010		0.36	4.8	1.7				0.85	3.9	8.9	1.1			
d) 1% _{mol} 1 in [C ₄ C ₁ Im][Tf ₂ N]															
Binding Energy / eV	74.2		688.8	686.8	402.1		399.5	293.0	287.7	286.8	285.3	169.1			
Nominal	0.010	0.020	6.1	0.12	2.0	0.020	1.0	2.0	1.0	4.2	3.0	0.020		4.0	2.0
Experimental, 0°	0.011		6.2	0.093	2.0		1.0	2.1	1.0	4.1	2.9			4.0	2.0
Experimental, 80°	0.012		6.9	0.039	1.9		0.97	2.1	0.93	3.8	3.2			3.7	2.0

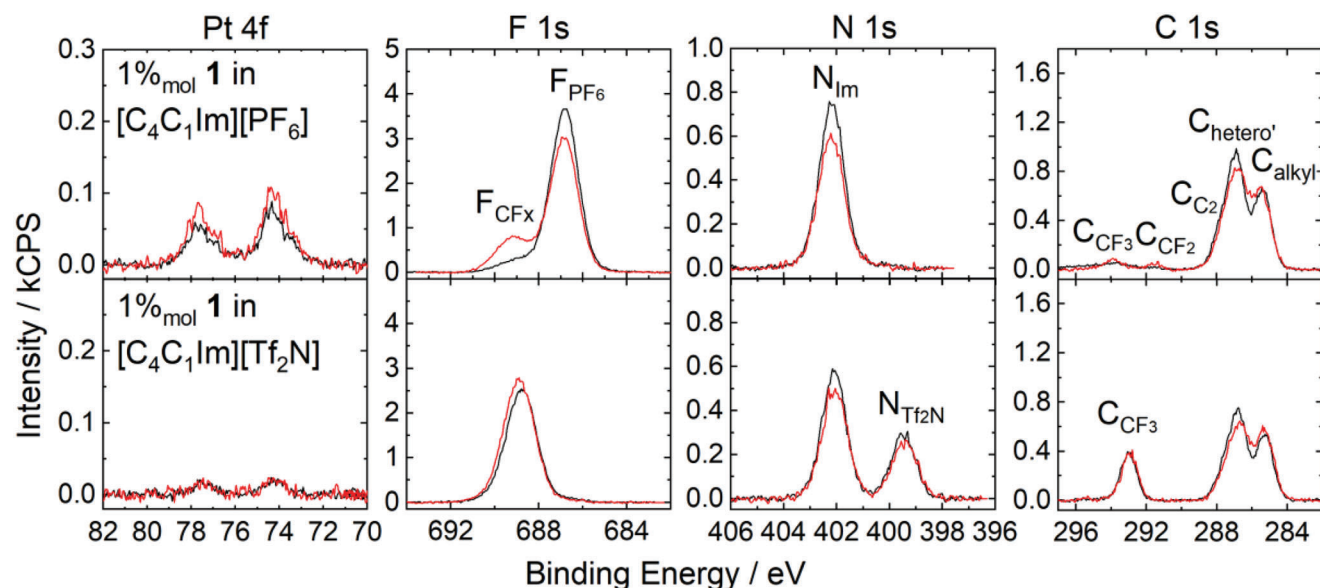


Figure 4. Pt 4f (left), F 1s (middle left), N 1s (middle right) and C 1s (right) XPS spectra of 1%_{mol} solutions of **1** in [C₄C₁Im][PF₆] (top) and [C₄C₁Im][Tf₂N] (bottom) in 0° (black) and 80° emission (red). For assignment of signals to the molecular structures see Figure 1. All spectra were recorded at room temperature.

to the different degree of surface enrichment of **1** in the different ILs. For the [C₂C₁Im][PF₆] solution, where the Pt signal shows the strongest enrichment, the C_{alkyl} signal at 0° and even more at 80° is much lower than nominally expected (Table 2a). For the [C₄C₁Im][PF₆] solution, close-to-nominal values are found at both angles (Table 2b), as has been discussed previously.^[11k] For [C₈C₁Im][PF₆], where no Pt enrichment is seen in Pt signal, the C_{alkyl} signal at 0° agrees well with the nominal one, and at 80° a significantly enhanced value is observed (Table 2c) which is in line with the absence of surface enrichment. The surface is thus dominated by the IL, with the topmost layer orientated such that the alkyl chain of the [C₈C₁Im]⁺ cation pointed toward the vacuum, as has been reported for the pure IL.^[10b]

Overall, we find that the surface enrichment of the catalyst in the [PF₆][−] ILs shows a strong dependence on the chain length of the alkyl substituent on the [C_nC₁Im]⁺ cation, which is due to the increasing surface affinity of longer alkyl chains competing with the fluorinated substituents. The latter effect translates into a lower surface tension, which will be correlated to the surface enrichment of **1** below.

Next, we will compare ARXP spectra of 1%_{mol} solutions of **1** in [C₄C₁Im][PF₆] (top) and [C₄C₁Im][Tf₂N] (bottom), that is, changing only the anion of the IL, shown in Figure 4. Comparing the Pt 4f signals clearly reveals for the [C₄C₁Im][PF₆] solution (green in Figure 3) a much higher intensity at both angles and with that a much higher surface concentration of **1** as compared to the [Tf₂N][−] solution (orange). As can be seen from the Pt 4f signals in Figure 3, the signal from the [C₄C₁Im][Tf₂N] solution (orange) shows a similar intensity as found for the [C₈C₁Im][PF₆] solution (blue) indicating homogeneous distribution of **1** at the surface also in [C₄C₁Im][Tf₂N]. This finding is supported by the quantitative analysis of the peak intensities shown in Table 2d, where the values experimentally derived from the 0° emission spectra agree well with the nominal composition. At 80°, the F_{CFx} signal of

[C₄C₁Im][Tf₂N] in Figure 4 shows a slight increase as compared to 0°, which is assigned to the orientation of **1** and the [Tf₂N][−] anion, as discussed above for the 10%_{mol} solution. The C_{alkyl} signal shows a slight increase at 80°, which is due to the orientation of the [C₄C₁Im]⁺ cation exposing its butyl chain toward the vacuum. This effect was not detected for the [C₄C₁Im][PF₆] solution due to the enrichment of **1** and the concomitant damping of the IL-specific C_{alkyl} signal.^[11k] For the [C₄C₁Im][Tf₂N] solution, all other signals show a slight decrease or remain constant at 80° corresponding to the preferred orientations of the ions at the surface, as discussed above. Note that for the very low-intense F_{PF6} signal a large uncertainty must be expected due to close vicinity to the intense F_{CFx} signal. With this, and also due to the absence of a sufficiently intense P 2p signal (due to its low concentration and cross-section), no conclusion about the interfacial behavior of the [PF₆][−] anion could be drawn at this concentration.

2.4. Correlating Surface Enrichment with the Surface Tension of the IL

In the following, we will address the correlation of concentration of **1** at the IL/vacuum interface with the surface tension of the neat IL solvents. The surface tension values γ were obtained by using the PD method under ultraclean vacuum conditions, and the values at 298 K are shown in Table 4 for all ILs investigated. The full sets of temperature-dependent surface tension measurements are depicted in Figure S13 (Supporting Information). The surface tensions of 34.2 mN m^{−1} for [C₈C₁Im][PF₆] and 43.4 mN m^{−1} for [C₄C₁Im][PF₆] were reported before by us, in good agreement with the literature data.^[10b,11k,14] For [C₂C₁Im][PF₆], we measured 51.9 mN m^{−1}. For this IL, Ref. [9c] denoted a value $\approx$ 50 mN m^{−1} at 298 K, without providing further information like the method used, the experimental

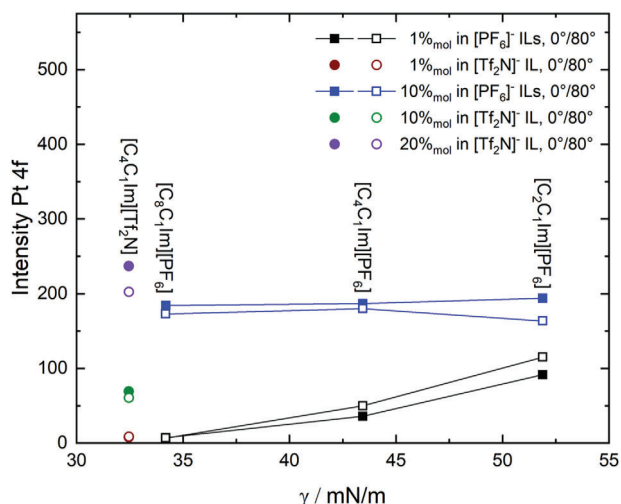


Figure 5. Total Pt 4f peak area detected in XPS of solutions of **1** with concentrations of 1%_{mol} in the [PF₆][−] ILs (black), 1%_{mol} in [C₄C₁Im][Tf₂N] (red brown), 10%_{mol} in the [PF₆][−] ILs (blue), 10%_{mol} in [C₄C₁Im][Tf₂N] (green) and 20%_{mol} in [C₄C₁Im][Tf₂N] (violet) in 0° (full symbols) and 80° emission (open symbols) against the surface tension γ of the neat ILs at 298 K. Note that for 1%_{mol} in [C₄C₁Im][Tf₂N] the signals for 0° (full) and 80° (open) fall on top of each other.

uncertainty, or additional references. Note that [C₂C₁Im][PF₆] is a solid at 298 K (melting point: 331–333 K^[18]). Nevertheless, we were able to measure the surface tension of this IL with our vacuum PD setup down to room temperature as a supercooled liquid (see [Experimental Section](#) for details). The same was possible also for the ultra-pure and surface-clean [C₄C₁Im][Cl] (melting point: 347 K^[19]) sample and we found a surface tension of 49.9 mN m^{−1} at 298 K, which is slightly higher than the value reported in literature of 48.2 mN m^{−1} using the capillary rise method.^[20] For [C₄C₁Im][Tf₂N], we obtained 32.5 mN m^{−1}, in excellent agreement with the literature data obtained by the PD method (32.5 mN m^{−1} at 298.15 K^[21]). The surface tension values at 298 K decrease in the following order: [C₂C₁Im][PF₆] > [C₄C₁Im][Cl] > [C₄C₁Im][PF₆] > [C₈C₁Im][PF₆] > [C₄C₁Im][Tf₂N] (see [Table 4](#)). In other words, the surface tension decreases with increasing chain length of the alkyl substituents for the [PF₆][−] ILs and, in terms of the anion with the same cation, in the order [Cl][−] > [PF₆][−] > [Tf₂N][−].

Figure 5 depicts the obtained absolute Pt 4f intensity of the solutions at 0° and 80° against the surface tension γ of the neat ILs at 298 K. For the three 10%_{mol} [PF₆][−] IL solutions, the Pt intensity is more or less identical at 80° (open blue squares) and also at 0° (full blue squares). For the 10%_{mol} [C₄C₁Im][Tf₂N] solution, the Pt intensity is much smaller (open and full green circles), as discussed above. At this concentration, the relatively high surface tension of the [PF₆][−] ILs facilitates strong enrichment of **1** at the IL/vacuum interface, while for [C₄C₁Im][Tf₂N] it is too low, such that enrichment of **1** does not result in sufficient lowering of the surface free energy. For the latter, only for a higher concentration of 20%_{mol} (open and full violet circles) surface enrichment occurs, as discussed above.

For the 1%_{mol} [PF₆][−] IL solutions (full and open black squares), the Pt 4f intensity increases with increasing surface tension of

the solvent, that is, the enrichment of the complex is strongest in the IL with the highest surface tension. For this IL, the strongest lowering in surface free energy is obtained by accumulation of the surface-active complex **1** at the IL/vacuum interface with respect to a reference situation where the complex would be homogeneously distributed in the surface-near region and in the bulk. For the solutions of [C₈C₁Im][PF₆] and also for [C₄C₁Im][Tf₂N] (full and open red brown circles), the surface activity of the solvent, induced by the long alkyl chains or the [Tf₂N][−] anions, respectively, is high enough to compete with the surface-active complex **1**, which results in a homogeneous distribution of solvent and solute in the surface-near region with no surface enrichment, as discussed above. Since the surface tension of [C₄C₁Im][Tf₂N] is lower than that of [C₈C₁Im][PF₆], one could anticipate surface depletion of **1** dissolved in the former, which was, however, not observed. It is possible that surface depletion of the catalyst occurs when being dissolved in an IL with an even lower surface tension.

2.5. Solutions of [C₃CNPFC₄Im][PF₆] in [C₄C₁Im][PF₆] and [C₄C₁Im][Cl]

As discussed above, the synthesis of **1** in [C₄C₁Im][Cl] was not successful. To nevertheless obtain some information on enrichment effects, we compare a 9.5%_{mol} solution of [C₃CNPFC₄Im][PF₆], which served as the surface-active ligand in **1**, in [C₄C₁Im][Cl] (top) to a 9.5%_{mol} solution in [C₄C₁Im][PF₆] (bottom). **Figure 6** depicts the corresponding F 1s, N 1s, and C 1s XP spectra; the full sets of spectra are shown in [Figures S14 and S15](#) (Supporting Information), and their quantitative analyses are provided in [Table 3a,b](#). The [PF₆][−] solution was studied in detail previously^[11k], with the ligand showing a significant, but lower surface enrichment as compared to **1**. Since the spectra of the [Cl][−] and [PF₆][−] solutions show many similarities, we only focus on the most important aspects: For both solutions, the ligand-specific F_{CFx} signals in [Figure 6](#) show a clear enhancement at 80° as compared to 0°, which is due to the surface enrichment of [C₃CNPFC₄Im][PF₆]. The increase for the [C₄C₁Im][Cl] solution (factor of 2.4) in [Figure 6](#) is more pronounced than for the [C₄C₁Im][PF₆] solution (factor of 2.0). Moreover, the signals stemming from both ligand and IL, that is, N_{Im}, C_{C2} and C_{hetero}, show a stronger decrease at 80° for the [C₄C₁Im][Cl] than for the [C₄C₁Im][PF₆] solution (see also [Table 3a,b](#)). Finally, while the IL-specific C_{alkyl} signals at 0° and 80° have very similar intensities for the [C₄C₁Im][PF₆] solution, a significantly smaller signal is seen at 80° for the [C₄C₁Im][Cl] solution. All these observations indicate that the enrichment of the solute at the IL/vacuum interface is more pronounced in [C₄C₁Im][Cl]. This is in line with the conclusion drawn above that employing a solvent with a higher surface tension, that is, 49.9 mN m^{−1} for [C₄C₁Im][Cl] vs 43.4 mN m^{−1} for [C₄C₁Im][PF₆] (see [Table 4](#)), results in a stronger surface enrichment of the solute.

3. Conclusion

We investigated the surface enrichment of a buoy-type catalyst **1** at the IL/vacuum interface in a variety of IL solvents, that is, [C₂C₁Im][PF₆], [C₄C₁Im][PF₆], [C₈C₁Im][PF₆], and

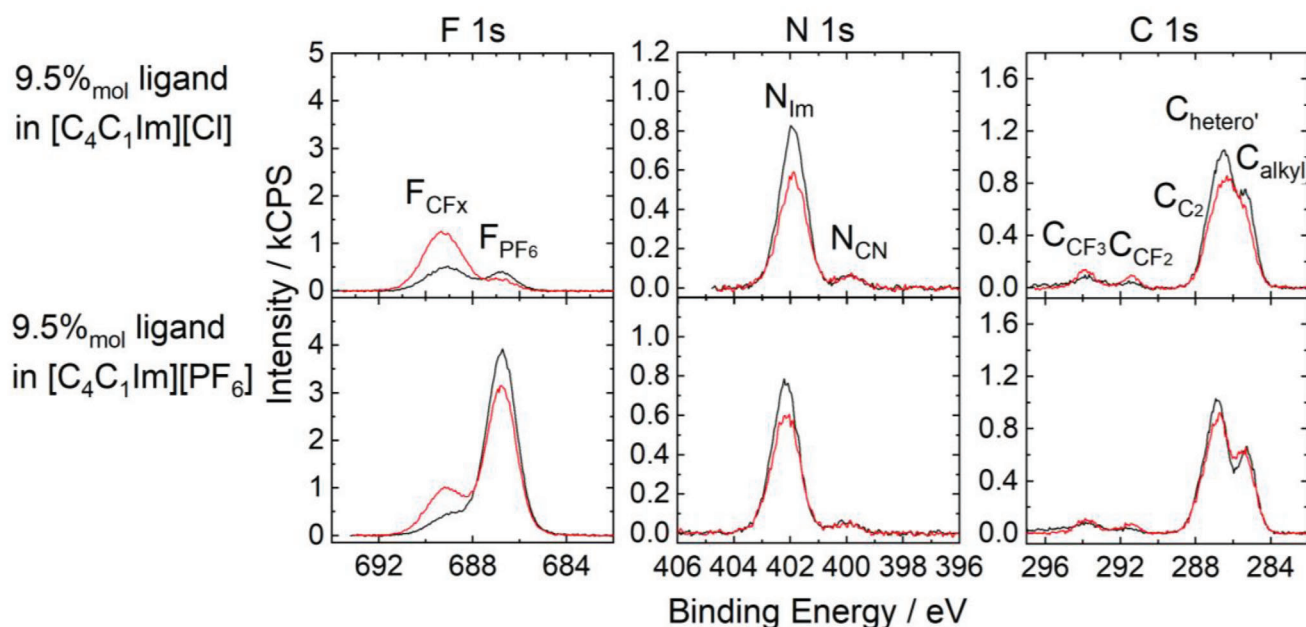


Figure 6. F 1s (left), N 1s (middle), and C 1s (right) XPS spectra of 9.5%_{mol} solutions of [C₃CNPF₆C₄Im][PF₆] in [C₄C₁Im][Cl] (top) and [C₄C₁Im][PF₆] (bottom) in 0° (black) and 80° emission (red). For assignment of signals to the molecular structures see Figure 1. All spectra were recorded at room temperature.

[C₄C₁Im][Tf₂N] using ARXPS. The catalyst was successfully prepared directly in the ILs [C₂C₁Im][PF₆], [C₈C₁Im][PF₆], and [C₄C₁Im][Tf₂N] by employing the same procedure reported previously in [C₄C₁Im][PF₆].^[11a,k]

For 10%_{mol} solutions of the catalyst in the [PF₆][−] ILs, we observed strong enrichment of the solute at the surface, which was found fully saturated with the complex. In [C₄C₁Im][Tf₂N], however, a homogeneous distribution of **1** at the surface and in the bulk was found in the 10%_{mol} solution with no surface enrichment, while for a 20%_{mol} solution, the surface was saturated with **1**. For dilute solutions with 1%_{mol} catalyst concentration, we observed for the [PF₆][−] ILs a pronounced increase in surface enrichment of **1** when decreasing the alkyl chain length at the cation. Moreover, we observe as general trend an increase of the surface enrichment with increasing surface tension value of the neat IL, that is, in the following order: [C₂C₁Im][PF₆] > [C₄C₁Im][PF₆] > [C₈C₁Im][PF₆] > [C₄C₁Im][Tf₂N]. The surface tension of [C₈C₁Im][PF₆] and [C₄C₁Im][Tf₂N] is even low enough to suppress the surface activity of **1**, resulting in homogeneous distribution of the solute, with no surface enrichment effects.

Since the formation of **1** in [C₄C₁Im][Cl] was not successful, we also investigated 9.5%_{mol} solutions of the neat ligand [C₃CNPF₆C₄Im][PF₆] in [C₄C₁Im][Cl] and [C₄C₁Im][PF₆]. In the latter, the ligand was previously also observed to be surface-active but to a lesser extent than **1**.^[11k] The enrichment of the ligand was found to be more pronounced in [C₄C₁Im][Cl], the IL with the higher surface tension, than in [C₄C₁Im][PF₆], which follows the correlation of the enrichment of the solute and the surface tension of the solvent found for the dissolved **1**.

Our results clearly demonstrate that, besides the parameters presented in previous studies,^[11a,k] the surface composition of an IL-based catalyst system strongly depends on the surface tension of the solvent, which can be tailored by modification of cation or

anion of the solvent IL. These results are highly interesting for the design of catalytic systems, where the interfacial structure can play a significant role for the efficiency of the process, such as in SILP catalysis. With the observed trends, tailoring the concentration of the catalyst at the IL/gas interface for optimum performance in specific transformations becomes realistic by choosing an IL or IL mixture with an appropriate surface tension.

4. Experimental Section

Materials and Sample Preparation: *Cis*-[PtCl₂(CH₃CN)₂] (purity 98%) was purchased from Sigma–Aldrich and used without further treatment. [C₈C₁Im][PF₆], [C₄C₁Im][Tf₂N] (both purity 99%), and [C₄C₁Im][Cl] (purity 99.5%) were purchased from Iolitec and, unless stated otherwise, used as delivered. [C₂C₁Im][PF₆] was purchased from Merck (for synthesis grade). The ARXPS analysis of this IL showed an unexpected O 1s peak at 532.1 eV, which increased at 80°, as well as a more intense C_{alkyl} signal than expected at 80° (not shown). These features were assigned to a significant amount of a surface-active contamination, and the IL was therefore cleaned by extraction using toluene. For this, ≈20 mL of [C₂C₁Im][PF₆] were heated to 80 °C (to ensure liquid state) and mixed with ≈1 mL of toluene (purity 99.8%) by vigorous stirring. After the phases separated upon rest, the toluene was removed, and the procedure repeated 10 times before drying the IL at 80 °C for several days. After this procedure, no unexpected signals were observed upon ARXPS analysis.

Complex **1** has shown significant beam damage in a 1%_{mol} solution in [C₄C₁Im][PF₆] in the presence of minor traces of iodine species, as discussed previously.^[11k] Therefore, for all 1%_{mol} solutions of **1** shown in this work (for preparation routes see below), water-cleaned ILs were used; the general cleaning procedure is detailed in Ref. [11k]. For [C₂C₁Im][PF₆] and [C₄C₁Im][Tf₂N], also for the more concentrated solutions the water-cleaning procedure was applied to the ILs prior to preparation of the catalyst solution. Note that ARXPS analysis of non-water-treated and water-treated neat ILs did not show significant differences; the ARXP spectra shown in Figure S1 (Supporting Information) were obtained from

Table 3. Quantitative analysis of XPS core level spectra of 9.5%_{mol} solutions of [C₃CNPFC₄Im][PF₆] in a) [C₄C₁Im][Cl] and b) in [C₄C₁Im][PF₆]. "Nominal" indicates the relative numbers of the atoms derived from the nominal stoichiometry, and "Experimental" the corresponding numbers deduced from the XPS data at 0° and 80°. For the spin-orbit-split signals, the indicated binding energy values correspond to larger peak, that is, Cl 2p_{3/2} and P 2p_{3/2}.

a) 9.5% _{mol} [C ₃ CNPFC ₄ Im][PF ₆] in [C ₄ C ₁ Im][Cl]	Cl 2p*	F 1s CFx	F 1s PF ₆	N 1s Im	N 1s CN	C 1s CF ₃	C 1s CF ₂	C 1s C ₂	C 1s hetero'	C 1s alkyl	P 2p*
Binding Energy / eV	197.3	689.1	686.8	401.9	399.9	293.9 (80°)	291.5 (80°)	287.4	286.5	285.2	136.7
Nominal	1.0	0.53	0.63	2.2	0.11	0.11	0.11	1.1	4.8	3.0	0.11
Experimental, 0°	0.99	1.1	0.60	2.2	0.15	0	0	1.1	5.1	2.4	0.12
Experimental, 80°	0.75	2.8	0.35	1.6	0.15	0.51	0.51	0.82	4.7	1.5	0.074
b) 9.5% _{mol} [C ₃ CNPFC ₄ Im][PF ₆] in [C ₄ C ₁ Im][PF ₆] ^[11k]											
Binding Energy / eV		688.8	686.8	402.2	400.0	293.9 (80°)	291.6 (80°)	287.7	286.8	285.3	136.8
Nominal		0.53	0.6	2.2	0.11	0.11	0.11	1.1	4.8	3.0	1.1
Experimental, 0°		1.1	0.6	2.1	0.16			1.1	4.7	2.7	1.2
Experimental, 80°		2.3	0.55	1.8	0.13	0.46	0.46	0.91	4.4	2.7	1.1

Table 4. Surface tension and density values at 298 K of neat [C₂C₁Im][PF₆], [C₄C₁Im][PF₆], [C₈C₁Im][PF₆], [C₄C₁Im][Tf₂N], and [C₄C₁Im][Cl] obtained from the PD method under vacuum conditions.

	Surface tension γ / mN m ⁻¹	Density ρ / g cm ⁻³
[C ₂ C ₁ Im][PF ₆]	51.89	1.47 ^[22]
[C ₄ C ₁ Im][PF ₆]	43.44 ^[11k]	1.36 ^[23]
[C ₈ C ₁ Im][PF ₆]	34.19 ^[10b]	1.24 ^[24]
[C ₄ C ₁ Im][Tf ₂ N]	32.46	1.44 ^[25]
[C ₄ C ₁ Im][Cl]	49.88	1.08 ^[26]

[C₂C₁Im][PF₆] treated with toluene and water. For the more concentrated solutions of the other ILs, no additional water-cleaning step was conducted since no beam damage effects were observed.

[C₂C₁Im][PF₆], and solutions of **1** in [C₂C₁Im][PF₆] and [C₄C₁Im][Cl] were solid at room temperature. For practical reasons, the samples containing these ILs were introduced into the load-lock of the ultra-high vacuum (UHV) chamber as hot liquids (T ≈ 80 °C). The catalyst solutions were introduced freshly after synthesis, while the neat ILs were first molten and stirred for ≈20 h at T = 100–120 °C before introducing them into the UHV system. The load-lock was immediately pumped down to vacuum conditions after introducing the IL-filled sample holders. With this procedure, the samples remained liquid in a supercooled state, so that acquisition of ARXP spectra in the liquid state was possible even at room temperature. The samples were left for degassing in the load-lock under UHV conditions for several hours. In case of spontaneous solidification upon evacuating the load-lock, the samples were molten again in the UHV chamber; after this, the samples remained liquid. As has been reported previously, owing to the slow diffusion in ILs, 10%_{mol} solutions were heated to T = 60 °C (T = 80 °C in [C₂C₁Im][PF₆]) and 1%_{mol} solutions to T = 40 °C (T = 80 °C in [C₂C₁Im][PF₆]) for ≈30 min and left for cooling down to room temperature prior to the ARXP analysis to ensure the thermodynamically favored surface structure.^[11a,k]

Complex **1** was synthesized in the respective ILs directly in the amount required to give the desired concentration; the procedure was described before for [C₄C₁Im][PF₆] as solvent^[11a,k] and was successfully expanded to several ILs in this work (see Results and Discussion). For the solutions of [C₂C₁Im][PF₆] and [C₄C₁Im][Cl], the ILs were added pre-degassed and in liquid state (T ≈ 80 °C) to the precursor mixture. All solutions of **1** were obtained clear and yellow–brown colored. Note that the 1%_{mol} solutions were prepared by simple dilution of freshly-prepared, more concentrated solutions (typically ≈10%_{mol}). The weighed amounts of materials for preparation of the solutions are shown in Table S4 (Supporting Information).

The preparation procedure was also attempted for a 20%_{mol} solution of **1** in [C₄C₁Im][Cl]. Upon adding the IL and heating to T = 100 °C under vacuum conditions, however, strong bubble formation, quick consumption of the remaining precursor material and coloring of the solution to deep red was observed. The solution was stirred for 3 h under these conditions to yield a clear, deep red-colored solution, which remained liquid even at room temperature. The reaction outcome is discussed in the Supporting Information.

ARXPS Measurements and Data Evaluation: Information on the experimental setup, and on the processing and evaluation of the XPS data is available in previous reports.^[11a,c,k] The unique dual analyzer for surface analysis (DASSA) setup is equipped with two analyzers mounted at an angle of 0° with respect to the surface plane (normal emission) and at 80° (grazing emission).^[27] The information depth (ID) of measurements in normal emission in IL-based samples is 6–9 nm, whereas at 80° it is only 1–1.5 nm.^[27] Therefore, the 80° spectra mainly reflect the composition of the topmost surface layer. In contrast to previous reports on related systems,^[11a,k] no normalization to the sum over all atomic sensitivity factor-corrected intensities was performed, which would account for potential changes of the photon flux between different measurement series. The spectra were fitted according to procedures reported before,^[11a,k]

with necessary additional information provided in the Supporting Information. For the ARXP spectra of neat $[C_4C_1Im][Cl]$, no referencing of the binding energy of the O^0 spectra was applied, since no F_{PF6} signal is present (all other spectra were referenced to the F_{PF6} signal at 686.8 eV in O^0 , as done in previous works).^[11a,k] With this, the binding energies of the neat IL excellently correspond to the solution, where synthesis of **1** was attempted in this IL shown in Figure S8 (Supporting Information). For the $[C_4C_1Im][Tf_2N]$ solutions, the spectra were referenced to the F_{CF_3} at 688.8 eV owing to the low intensity of the F_{PF6} signal.

Pendant Drop Measurements: The surface tension of the neat ILs was determined using our novel high vacuum setup, which was described in detail previously.^[14] The uncertainty of the surface tension was obtained from this setup to $\pm 0.1\%$ ($\pm 0.04 \text{ mN m}^{-1}$);^[14] the uncertainty therefore lies within the size of the data points shown in Figure 5.

The typical procedure for introducing the ILs was outlined before for room temperature ILs.^[14] To avoid rapid release of dissolved gases upon melting of $[C_2C_1Im][PF_6]$ and $[C_4C_1Im][Cl]$ (which are solid at room temperature) during the degassing procedure in the high vacuum setup, the ILs were pre-degassed by stirring under reduced pressure for several hours at $T \approx 100\text{--}120^\circ\text{C}$ in a Schlenk-tube. The hot liquids were then introduced into the IL reservoir and the chamber was immediately pumped down to vacuum conditions and heated for further degassing the ILs (final pressure $\approx 10^{-6}$ mbar).^[14] The measurements were started at high temperature and gradually allowed to cool toward room temperature. $[C_2C_1Im][PF_6]$ and $[C_4C_1Im][Cl]$ remained in a supercooled state over the whole period of the temperature-dependent surface tension measurements so that data points could be taken even at room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. Source data are provided at Zenodo: DOI 10.5281/zenodo.10977887.

Keywords

materials properties, Pt catalyst, supported ionic liquid phase catalysis (SILP), surface enrichment, X-ray photoelectron spectroscopy

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- [1] a) P. Lanzafame, S. Perathoner, G. Centi, S. Gross, E. J. M. Hensen, *Catal. Sci. Technol.* **2017**, *7*, 5182; b) J. García-Serna, R. Piñero-Hernanz, D. Durán-Martín, *Catal. Today* **2022**, *387*, 237.

- [2] A. Wang, J. Li, T. Zhang, *Nat. Rev. Chem.* **2018**, *2*, 65.
[3] X. Deng, J. Wang, N. Guan, L. Li, *Cell Rep. Phys. Sci.* **2022**, *3*, 101017.
[4] O. Piematti, R. Abu-Reziq, L. Vaccaro, in *Catalyst Immobilization* (Eds.: M. Benaglia, A. Puglisi), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany **2020**, pp. 1–22.
[5] a) J. M. Marinkovic, A. Riisager, R. Franke, P. Wasserscheid, M. Haumann, *Ind. Eng. Chem. Res.* **2019**, *58*, 2409; b) A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Eur. J. Inorg. Chem.* **2006**, *2006*, 695; c) A. Riisager, B. Jørgensen, P. Wasserscheid, R. Fehrmann, *Chem. Commun.* **2006**, 994.
[6] P. Latos, A. Wolny, A. Chrobok, *Materials* **2023**, *16*, 2106.
[7] a) V. I. Părvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615; b) T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459; c) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508; d) C. Dai, J. Zhang, C. Huang, Z. Lei, *Chem. Rev.* **2017**, *117*, 6929.
[8] H.-P. Steinrück, P. Wasserscheid, *Catal. Lett.* **2015**, *145*, 380.
[9] a) C. S. Santos, S. Baldelli, *Chem. Soc. Rev.* **2010**, *39*, 2136; b) H.-P. Steinrück, *Phys. Chem. Chem. Phys.* **2012**, *14*, 5010; c) M. Tariq, M. G. Freire, B. Saramago, J. A. P. Coutinho, J. N. C. Lopes, L. P. N. Rebelo, *Chem. Soc. Rev.* **2012**, *41*, 829; d) Y.-L. Wang, B. Li, S. Sarman, F. Mocchi, Z.-Y. Lu, J. Yuan, A. Laaksonen, M. D. Fayer, *Chem. Rev.* **2020**, *120*, 5798; e) Z. Zhai, U. Paap, A. Gezmis, F. Maier, H.-P. Steinrück, T. M. Koller, *J. Mol. Liq.* **2023**, *386*, 122388; f) K. R. J. Lovelock, I. J. Villar-Garcia, F. Maier, H.-P. Steinrück, P. Licence, *Chem. Rev.* **2010**, *110*, 5158; g) I. J. Villar-Garcia, S. Fearn, N. L. Ismail, A. J. S. McIntosh, K. R. J. Lovelock, *Chem. Commun.* **2015**, *51*, 5367; h) Q. Huang, Y. Huang, Y. Luo, L. Li, G. Zhou, X. Chen, Z. Yang, *Phys. Chem. Chem. Phys.* **2020**, *22*, 13780; i) R. Costa, C. M. Pereira, A. F. Silva, P.-F. Brevet, E. Benichou, *J. Phys. Chem. B* **2020**, *124*, 3954; j) E. J. Smoll Jr., S. M. Purcell, L. D'Andrea, J. M. Slattery, D. W. Bruce, M. L. Costen, K. G. McKendrick, T. K. Minton, *J. Phys. Chem. Lett.* **2019**, *10*, 156; k) E. J. Smoll, M. A. Tesa-Serrate, S. M. Purcell, L. D'Andrea, D. W. Bruce, J. M. Slattery, M. L. Costen, T. K. Minton, K. G. McKendrick, *Faraday Discuss.* **2018**, *206*, 497; l) K. Nakajima, M. Lísál, K. Kimura, in *Surface and Interface Science*, Vol. 7 (Ed.: K. Wandelt), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany **2020**, pp. 351–389; m) K. Nakajima, M. Miyashita, M. Suzuki, K. Kimura, *J. Chem. Phys.* **2013**, *139*, 224701.
[10] a) B. S. J. Heller, M. Lexow, F. Greco, S. Shin, G. Partl, F. Maier, H.-P. Steinrück, *Chemistry* **2020**, *26*, 1117; b) U. Paap, V. Seidl, K. Meyer, F. Maier, H.-P. Steinrück, *Molecules* **2022**, *27*, 8561; c) V. Lockett, R. Sedev, S. Harmer, J. Ralston, M. Horne, T. Rodopoulos, *Phys. Chem. Chem. Phys.* **2010**, *12*, 13816; d) E. F. Smith, F. J. M. Rutten, I. J. Villar-Garcia, D. Briggs, P. Licence, *Langmuir* **2006**, *22*, 9386; e) S. Men, B. B. Hurriso, K. R. J. Lovelock, P. Licence, *Phys. Chem. Chem. Phys.* **2012**, *14*, 5229; f) E. Oz, O. Sahin, H. I. Okur, S. Suzer, *ChemPhysChem* **2020**, *21*, 2397; g) N. Calisi, S. Martinuzzi, A. Giaccherini, C. S. Pomelli, L. Guazzelli, S. Caporali, *J. Electron Spectrosc. Relat. Phenom.* **2021**, *247*, 147034; h) S. Caporali, M. Pedio, C. Chiappe, C. S. Pomelli, R. G. Acres, U. Bardi, *Surf. Sci.* **2016**, *648*, 360; i) Y. Zhang, Y. Khalifa, E. J. Maginn, J. T. Newberg, *J. Phys. Chem. C* **2018**, *122*, 27392.
[11] a) D. Hemmeter, D. Kremitzl, P. S. Schulz, P. Wasserscheid, F. Maier, H.-P. Steinrück, *Chem.-Eur. J.* **2023**, *29*, e202203325; b) D. Hemmeter, U. Paap, F. Maier, H.-P. Steinrück, *Catalysts* **2023**, *13*, 871; c) D. Hemmeter, U. Paap, N. Taccardi, J. Mehler, P. S. Schulz, P. Wasserscheid, F. Maier, H.-P. Steinrück, *ChemPhysChem* **2023**, *24*, 202200391; d) E. J. Smoll, X. Chen, L. M. Hall, L. D'Andrea, J. M. Slattery, T. K. Minton, *J. Phys. Chem. C* **2020**, *124*, 382; e) A. Dimitrova, M. Walle, M. Himmerlich, S. Krischok, *J. Mol. Liq.* **2017**, *226*, 78; f) T. Kurisaki, D. Tanaka, Y. Inoue, H. Wakita, B. Minofar, S. Fukuda, S.-i. Ishiguro, Y. Umehayashi, *J. Phys. Chem. B* **2012**, *116*, 10870; g) S. Men, J. Jiang, *Chem. Phys. Lett.* **2016**, *646*, 125; h) S. Men, J. Jiang, *Russ. J. Phys. Chem. A* **2018**, *92*, 1627; i) S. Men, Y. J. Jin, *Russ. J. Phys. Chem. A* **2018**, *92*, 2472; j) S. Men, K. R. J. Lovelock, P. Licence,

- RSC Adv. **2015**, 5, 35958; k) D. Hemmeter, U. Paap, N. Wellenhofer, A. Gezmis, D. Kremitzl, P. Wasserscheid, H.-P. Steinrück, F. Maier, *ChemPhysChem* **2023**, 24, 202300612.
- [12] a) F. Maier, J. M. Gottfried, J. Rossa, D. Gerhard, P. S. Schulz, W. Schwieger, P. Wasserscheid, H.-P. Steinrück, *Angew. Chem., Int. Ed.* **2006**, 45, 7778; b) C. Kolbeck, N. Paape, T. Cremer, P. S. Schulz, F. Maier, H.-P. Steinrück, P. Wasserscheid, *Chem.-Eur. J.* **2010**, 16, 12083; c) C. Kolbeck, N. Taccardi, N. Paape, P. S. Schulz, P. Wasserscheid, H.-P. Steinrück, F. Maier, *J. Mol. Liq.* **2014**, 192, 103.
- [13] F. Maier, T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, P. S. Schulz, P. Wasserscheid, H. P. Steinrück, *Phys. Chem. Chem. Phys.* **2010**, 12, 1905.
- [14] U. Paap, B. Krell, H.-P. Steinrück, F. Maier, *Int. J. Mol. Sci.* **2022**, 23, 13158.
- [15] K. R. J. Lovelock, C. Kolbeck, T. Cremer, N. Paape, P. S. Schulz, P. Wasserscheid, F. Maier, H. P. Steinrück, *J. Phys. Chem. B* **2009**, 113, 2854.
- [16] a) K. Nakajima, A. Ohno, M. Suzuki, K. Kimura, *Langmuir* **2008**, 24, 4482; b) A. Sanmartín Pensado, P. Malfreyt, A. A. H. Pádua, *J. Phys. Chem. B* **2009**, 113, 14708; c) T. Iwahashi, T. Miyamae, K. Kanai, K. Seki, D. Kim, Y. Ouchi, *J. Phys. Chem. B* **2008**, 112, 11936.
- [17] a) R. Souda, *Surf. Sci.* **2010**, 604, 1694; b) K. Nakajima, S. Nakanishi, M. Lísál, K. Kimura, *J. Mol. Liq.* **2017**, 230, 542; c) K. Nakajima, S. Oshima, M. Suzuki, K. Kimura, *Surf. Sci.* **2012**, 606, 1693; d) B. S. J. Heller, C. Kolbeck, I. Niedermaier, S. Dommer, J. Schatz, P. Hunt, F. Maier, H.-P. Steinrück, *ChemPhysChem* **2018**, 19, 1733.
- [18] J. Fuller, R. T. Carlin, H. C. De Long, D. Haworth, *J. Chem. Soc., Chem. Commun.* **1994**, 299.
- [19] A. Efimova, G. Hubrig, P. Schmidt, *Thermochim. Acta* **2013**, 573, 162.
- [20] M. H. Ghatee, A. R. Zolghadr, *Fluid Phase Equilib.* **2008**, 263, 168.
- [21] M. Geppert-Rybczyńska, J. K. Lehmann, J. Safarov, A. Heintz, *J. Chem. Thermodyn.* **2013**, 62, 104.
- [22] C. M. S. S. Neves, K. A. Kurnia, K. Shimizu, I. M. Marrucho, L. P. N. Rebelo, J. A. P. Coutinho, M. G. Freire, J. N. Canongia Lopes, *Phys. Chem. Chem. Phys.* **2014**, 16, 21340.
- [23] J. Jacquemin, P. Husson, A. A. H. Padua, V. Majer, *Green Chem.* **2006**, 8, 172.
- [24] R. L. Gardas, M. G. Freire, P. J. Carvalho, I. M. Marrucho, I. M. A. Fonseca, A. G. M. Ferreira, J. A. P. Coutinho, *J. Chem. Eng. Data* **2007**, 52, 80.
- [25] C. A. Nieto de Castro, E. Langa, A. L. Morais, M. L. M. Lopes, M. J. V. Lourenço, F. J. V. Santos, M. S. C. S. Santos, J. N. C. Lopes, H. I. M. Veiga, M. Macatrão, J. M. S. S. Esperança, C. S. Marques, L. P. N. Rebelo, C. A. M. Afonso, *Fluid Phase Equilib.* **2010**, 294, 157.
- [26] J. Li, H. Zhu, C. Peng, H. Liu, *Chin. J. Chem. Eng.* **2019**, 27, 2994.
- [27] I. Niedermaier, C. Kolbeck, H.-P. Steinrück, F. Maier, *Rev. Sci. Instrum.* **2016**, 87, 045105.