New Guanidinium-based Room-temperature Ionic Liquids. Substituent and Anion Effect on Density and Solubility in Water

Milen G. Bogdanov[a,c], Desislava Petkova[a,c], Stanimira Hristeva[a,c], Ivan Svinyarov[a,c], and Willi Kantlehner[b,c]

[a] Faculty of Chemistry, University of Sofia, 1, J. Bourchier Blvd., 1164 Sofia, Bulgaria
[b] Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany
[c] Fakultät Chemie/Organische Chemie, Hochschule Aalen, Beethovenstraße 1, 73430 Aalen, Germany

Reprint requests to Dr. Milen G. Bogdanov. E-mail: mbogdanov@chem.uni-sofia.bg

Z. Naturforsch. **2010**, *65b,* 37 – 48; received October 28, 2009

Dedicated to Professor Klaus Peseke on the occasion of his 70th birthday

In order to examine the influence of the alkyl chain length on some physical properties of guanidinium salts, the synthesis of a homologous series of new *N*″-*n*-alkylsubstituted *N*,*N*-diethyl-*N*′,*N*′-di-*n*-propyl-*N*″-*n*-hexyl guanidinium ionic liquids (gILs), containing chloride (Cl), tetrafluoroborate (BF_4), acesulfamate (Ace), saccharinate (Sac), and tosylate (Tos) as anions, is reported. **C_n-gILAce**, **C_n-gILSac**, and **C_n-gILBF$_4$** were obtained by ion exchange reaction of the corresponding hexasubstituted guanidinium chlorides (**C_n-gCl**, n = 3, 4, 6, 8, 10), which were synthesized by a quaternization reaction of the pentaalkyl-substituted guanidine **3** and the corresponding alkylchloride in DMF. The tosylates gILs **C_n-gTos** (n = 1, 2, 4, 6, 8, 10) were synthesized by alkylation of **3** with the corresponding alkyltosylates. Some physical properties, such as solubility in water and organic solvents, refractive index and density, are considered as a function of the length of the *n*-alkyl substituent R and the nature of the anion.

Key words: Ionic Liquids, Guanidinium Salts, Density, Quaternization Reaction, DMF

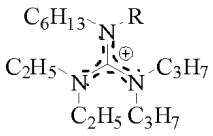
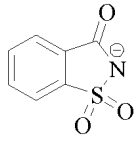
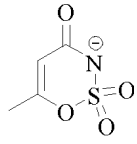
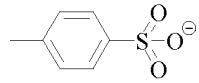
Introduction

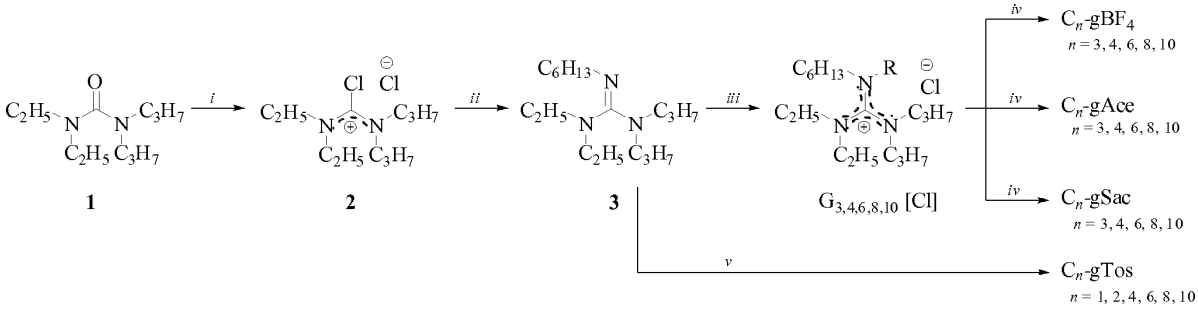
Room-temperature ionic liquids (RTILs) have attracted enormously the attention of the scientific community in the last two decades. Consisting entirely of ions (normally a small organic cation and an inorganic or organic anion), they are liquids at ambient temperature and display high thermal and chemical stability, a large electrochemical window, high ionic conductivity, relatively low viscosity and negligible vapor pressure. Furthermore, depending on the ion combination, they can be soluble or insoluble in water or organic solvents, respectively. These unique physico-chemical properties favor their application in diverse fields such as synthesis [1a], catalysis [1b], electrochemistry [1c], nanotechnology [1d], separation technology, and analytical chemistry [1e], *etc*.

Along with ILs based on 1,3-dialkylimidazolium cations, which seem to dominate the ILs area, ILs based on tetraalkylammonium, sulfonium, phosphonium and pyrrolidinium cations have been extensively studied. In contrast, the knowledge on the synthesis, physical properties and potential application of ILs based on the guanidinium ion is quite rare. A retrospective view on guanidinium ILs (gILs) in the last decade shows the availability of only a few published reports: two examples of iodide and tricyanomethanide $(NC)_3C^-$ gILs were used for dye-sensitized solar cells [2]; series of gILs, including cyclic representatives, based on NO_3^-, ClO_4^- and $(NO_2)_2N^-$ anions were synthesized as high-energy ILs by Schreeve and coworkers [3]; several examples of dimethyltetraalkyl gILs-based on BF_4^-, PF_6^-, NTf_2^-, Sac^-, and $N(CN)_2^-$ anions have been reported as a new generation of RTILs by Afonso and coworkers [4a, b]; more than thirty hexaalkylguanidinium trifluoromethanesulfonates (TfO^-) have been reported by Kunkel and Maas [5], and new chiral hexasubstituted RTgILs by Afonso and coworkers [4c] and Shah and Liebscher [6]; very recently, a series of (bis(trifluoromethylsulfonyl)imide) (Tf_2N^-) gILs have been reported by Yang and coworkers [7a, b] as poten-

0932–0776 / 10 / 0100–0037 $ 06.00

Table 1. Structure and abbreviation of the synthesized RTILs based on *N*″-*n*-alkyl-substituted *N*,*N*-diethyl-*N*′,*N*′-di-*n*-propyl-*N*″-*n*-hexyl guanidinium cations (**C*n*-g$^+$**).

C_n-g$^+$	Cloride Cl^-	Tetrafluoroborate BF_4^-	Saccharinate Sac^-	Acesulfamate Ace^-	Tosylate Tos^-
					
R = CH_3-	–	–	–	–	C_1-gTos
R = C_2H_5-	–	–	–	–	C_2-gTos
R = C_3H_7-	C_3-gCl	C_3-gBF_4	C_3-gSac	C_3-gAce	–
R = C_4H_9-	C_4-gCl	C_4-gBF_4	C_4-gSac	C_4-gAce	C_4-gTos
R = C_5H_{13}-	C_6-gCl	C_6-gBF_4	C_6-gSac	C_6-gAce	C_6-gTos
R = C_8H_{17}-	C_8-gCl	C_8-gBF_4	C_8-gSac	C_8-gAce	C_8-gTos
R = $C_{10}H_{21}$-	C_{10}-gCl	C_{10}-gBF_4	C_{10}-gSac	C_{10}-gAce	C_{10}-gTos



Scheme 1. Synthesis of guanidinium RTILs. Reagents and conditions: (*i*) $COCl_2/CH_3CN$, −25 °C to r. t., 24 h (yield 98 %); (*ii*) **2** in $CH_3CN/H_2NC_6H_{13}$, −10 °C to r. t., 16 h (yield 80 %); (*iii*) RCl/DMF, 100 – 110 °C, 10 – 13 h (yield 30 – 87 %); (*iv*) MeOH or water/K or Na salt of the corresponding anion, 60 °C, 4 h (yield 82 – 99 %); (*v*) TosR/DMF, 100 – 110 °C, 2 – 4 h (yield 83 – 99 %).

tial new electrolytes for lithium batteries, and a new cyclic guanidinium ionic liquid OGI (1,3-dimethyl-2-*N*″-methyl-*N*″-octylimidazoguanidinium iodide) was used as a quasi-solid-state electrolyte for dye-sensitized solar cells by Li *et al.* [8]. It should further be mentioned that as a result of finding a new protocol for the synthesis of hexasubstituted guanidinium salts [9a – d], Kantlehner *et al.* in 1984 were able to synthesize a large number (more than hundred) of hexaalkylguanidinium salts [9e], which in two cases have been described as oils. Nevertheless, considering the great versatility of the guanidinium cation (we have calculated more than 10^5 possible combinations if one varies the alkyl substituents from methyl to dodecyl in the guanidinium ion) the above contributions represent a "drop in the ocean" in the field of guanidinium-based ILs, or in the ILs area in general. Having in mind this incredible number, a lot of work impends upon the development of new synthetic methods for gILs and the investigation of their properties and potential industrial applications.

In this direction, in order to investigate the influence of the anions and the chain length of the alkyl substituents on some physical properties, here we report the synthesis of a series of hydrophobic room-temperature hexaalkylguanidinium ionic liquids (**C*n*-gX**), containing chloride (Cl), tetrafluoroborate (BF_4), acesulfamate (Ace), saccharinate (Sac), and tosylate (Tos) as anions X (Table 1).

Results and Discussion

Synthesis of compounds

The synthesis of the guanidinium salts is presented in Scheme 1. *N*,*N*-diethyl-*N*′,*N*′-di-*n*-propylurea **1**, the corresponding chloroformamidinium chloride **2** and guanidine **3** were synthesized as previously described by Kantlehner and coworkers [2, 9a – e]. In order to synthesize guanidinium halides for anion metathesis reactions, guanidine **3** was further quaternized with chloroalkanes instead of bromo- or iodo-substituted analogs. It is known [10] that the bromoalkanes re-

Table 2. Abbreviations, molecular weights, densities, water content, water uptake ability, and solubility in water and some organic solvents of the synthesized RTgILs evaluated in this study.

Compound	M_w	ρ_{dried}[a]	Water content[b]	Water uptake[c]	Solubility[d]	
	($g\,mol^{-1}$)	($g\,mL^{-1}$)	(ppm)	(wt-%)	immiscible	miscible
C_3-gCl	362.04	–	670	soluble	de, ch, bme	w, et, dcm, ac
C_4-gCl	376.06	0.949	690	soluble	de, ch, bme	w, et, dcm, ac
C_6-gCl[e]	404.12	–	–	soluble	de, ch, bme	w, et, dcm, ac
C_8-gCl	432.17	0.931	720	soluble	de, ch, bme	w, et, dcm, ac
C_{10}-gCl	460.22	0.929	600	soluble	w, ch	et, dcm, ac de, bme
C_3-gBF_4	413.39	1.011	370	5.21	w, de, ch, bme	et, dcm, ac
C_4-gBF_4	427.41	1.009	330	4.36	w, de, ch, bme	et, dcm, ac
C_6-gBF_4	455.77	0.997	350	3.19	w, de, ch, bme	et, dcm, ac
C_8-gBF_4	483.52	0.990	330	3.03	w, de, ch, bme	et, dcm, ac
C_{10}-gBF_4	511.57	0.981	300	2.88	w, de, ch, bme	et, dcm, ac
C_3-gAce	488.73	1.056	390	20.64	w, de, ch, bme	et, dcm, ac
C_4-gAce	502.75	1.050	406	17.77	w, de, ch, bme	et, dcm, ac
C_6-gAce	530.81	1.031	420	12.55	w, de, ch, bme	et, dcm, ac
C_8-gAce	558.86	1.022	350	10.88	w, de, ch, bme	et, dcm, ac
C_{10}-gAce	586.45	1.005	360	10.35	w, de, ch, bme	et, dcm, ac
C_3-gSac	508.76	1.069	520	24.77	w, de, ch, bme	et, dcm, ac
C_4-gSac	522.79	1.063	400	15.31	w, de, ch, bme	et, dcm, ac
C_6-gSac	550.84	1.045	420	12.73	w, de, ch, bme	et, dcm, ac
C_8-gSac	578.89	1.041	350	9.15	w, de, ch, bme	et, dcm, ac
C_{10}-gSac	606.95	1.024	360	10.46	w, de, ch, bme	et, dcm, ac
C_1-gTos	469.72	1.045	650	soluble	de, ch, bme	w,et, dcm, ac
C_2-gTos	483.75	1.035	740	soluble	de, ch, bme	w, et, dcm, ac
C_4-gTos	511.38	1.027	750	soluble	de, ch, bme	w, et, dcm, ac
C_6-gTos	539.86	1.014	350	26.78	w, de, ch, bme	et, dcm, ac
C_8-gTos	567.91	1.001	300	23.69	w, de, ch, bme	et, dcm, ac
C_{10}-gTos	595.96	0.989	450	15.93	w, de	et, dcm, ac, ch, bme

[a] Measured at 25 °C; [b] water content estimated prior to the measurements; [c] measured at 25 °C; [d] observed two phases (immiscible) and complete solubilization (miscible), where: de – diethyl ether, ch – cyclohexane, bme – butyl methyl ether, w – water, et – ethanol, dcm – dichloromethane, ac – acetone; [e] not liquid at r. t.

act strongly exothermic as the reaction rate increases, which is a disadvantage for large-scale experiments. The reaction with iodoalkanes can be often carried out at room temperature, but the formed iodide salts are light-sensitive. Moreover, the solubility of many inorganic salts M^+X^- in water decreases in the order $Cl^- < Br^- < I^-$, which has a high impact on the anion exchange reaction. It seems that the only disadvantage of using chloroalkanes in this important step is the prolonged reaction time of 2 – 3 d [11]. To overcome this problem, appropriate reaction conditions that can accelerate the reaction and increase the yields must be found.

Although different solvents might be used in the quaternization step, the reaction for the ILs purpose is normally carried out under solvent-free conditions, *i. e.* the two reagents are mixed and heated to give two phases. Furthermore, from the recently reported [12] comparative study on the rate of single-phase and two-phase synthesis of BumimCl it can be concluded that the rate of a stirred solvent-free reaction is almost the same as that in a single-phase system containing 20 vol-% ethanol, which shows that there is no particular advantage in using solvents. On the other hand, it is well known that the nucleophilic substitution reactions (S_N) are accelerated in more polar solvents in the case of uncharged species reacting to charged ones [13]. On this basis, it could be assumed that the use of relatively highly polar DMF (dielectric constant = 38.3, b. p. 153 °C) as solvent in the quaternizaton step will accelerate the reaction. To prove the validity of this assumption, independent reactions between the pentasubstituted guanidine **3** and BuCl as reference compounds were carried out on the 0.013 molar scale. Each reaction mixture was heated at 110 °C (oil bath) for the appropriate reaction time, worked up, and the yields were estimated. Using this strategy we found that **3** reacts with BuCl in 89 % yield within 13 h. A prolongation of the reaction time does not lead to a significant improvement in yield. Thus, the quaternization

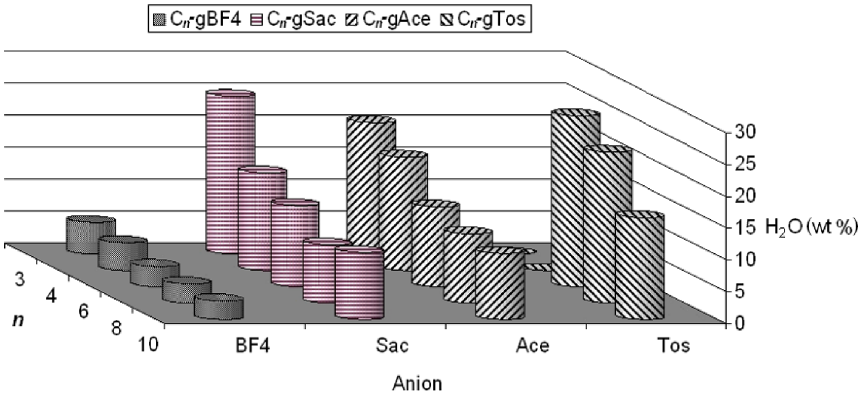


Fig. 1. Solubility of water in **C_n-gILs** as a function of the nature of the anions and the number of carbon atoms in the alkyl chain *n* at room temperature.

reactions of guanidine **3** with butyl, hexyl, octyl, and decyl chloride on a larger scale (0.1 mol) were carried out with a threefold molar excess of the corresponding alkyl chloride at 100 – 110 °C in DMF as solvent for approximately 13 h. IR spectroscopy proved to be a good method for monitoring the reaction in this case, since the disappearance of the C=N band of **3** at about 1610 cm^{-1} and the appearance of a C^+–N band of **C_n-gCl** at about 1530 cm^{-1} can be easily observed. Thus, **C_n-gCl** (n = 4, 6, 8, 10) were obtained in 80 – 90 % yields. It should be mentioned that the successful progress of the reaction is limited to a certain temperature range. A reaction temperature above 110 °C results in a reversion of the quaternization reaction (detected by IR spectroscopy), and the use of temperatures lower than 80 °C results in significant prolongation of the reaction time, and thus in lowering the yields. Limited by the boiling point of propyl chloride (b. p. 46.7 °C), the quaternization reaction in this case was carried out at 60 °C and with a greater excess of the latter (added portionwise), leading to the formation of **C_3-gCl** in 30 % yield.

As can be seen from Table 2, all of the synthesized hexaalkylguanidinium chlorides are miscible with water and immiscible with diethyl ether or cyclohexane. This allows their isolation and purification by dissolving each product in a small quantity of water and subsequent extraction of the residual volatile organic components. This approach was very useful, especially in the case of high-boiling alkyl chlorides. Except for **C_6-gCl**, which crystallized spontaneously after drying under vacuum, the other guanidinium chlorides **C_n-gCl** (n = 3, 4, 8, 10) are liquids at room temperature.

The synthesis of tetrafluoroborate (BF_4), acesulfamate (Ace) and saccharinate (Sac) gILs was achieved by metathesis reactions of **C_n-gCl** with the corresponding sodium or potassium salt in methanol or water as solvents. The tosylate series was synthesized by alkylation of guanidine **3** with the corresponding tosylate. The reactions were carried out under the quaternization conditions described above, but with a smaller excess (1.1 equiv.) of the tosyl ester. In all cases the reactions proceeded quantitatively within 4.5 h. All synthesized compounds were characterized by spectroscopic methods (^1H, ^{13}C NMR, IR), and the purity was established by elemental analysis. Furthermore, some properties of the synthesized gILs, such as miscibility with organic solvents, water uptake ability and density, were assessed as a function of the anion and of the chain length of the alkyl substituent.

Properties

Table 2 shows molecular weights, densities, water content, water uptake ability, and solubility in solvents of the synthesized RTgILs. For water-insoluble gILs, the water content prior to the property measurement was estimated (by Karl-Fischer titration) to be in the range 300 to 550 ppm and between 600 and 750 ppm for the water soluble **C_n-gCl** (n = 3, 4, 6, 8, 10) and **C_n-gTos** (n = 1, 2, 4). It is noteworthy that all **C_n-gILs** are strongly hygroscopic. The capacity to absorb water from the air was found to depend of course on the relative atmospheric humidity, but also on the length of the alkyl substituent R. The absorbed water is readily released by heating under vacuum, and thus, the synthesized RTgILs might be considered as desiccants.

The compounds studied are, however, stable in the air and in common organic solvents such as methanol, acetone, dichloromethane, chloroform, and acetonitrile, in which they are completely soluble. Furthermore, they are insoluble (formation of two phases is

observed) in cyclohexane, diethyl ether and water, but their miscibility with the latter depends not only on the hydrophobicity of the cation, but also on the nature of the anion and the temperature. These exceptional solubility characteristics in general make them good candidates for multiphasic reactions, liquid extraction and separation technology [14, 15]. To examine the affinity for the absorption of water, equivalent quantities of the corresponding hydrophobic gIL and water were shaken vigorously in a closed tube, and then the water content in the IL layer was estimated by Karl-Fischer titration. Fig. 1 presents the water content of the water-saturated **C_n-gILs** in wt-%. The observed decrease in water uptake ability with increasing number n of the carbon atoms in the alkyl chain clearly shows that the alkyl chain length corresponds to the hydrophobicity. On the other hand, the nature of the anion controls the hydrophobicity as well. Regarding the influence of the anion, the water uptake ability decreases as follows: **C_n-gTos** > **C_n-gAce** ≈ **C_n-gSac** > **C_n-gBF_4**. This sequence can be rationalized by taking into account the basicity of the corresponding anions. Furthermore, three immiscible liquid layers were obtained by mixing water, cyclohexane or diethyl ether, and selected gILs. The formation of a sequence water/gIL/diethyl ether depends clearly on the density of the ILs under study. Thus, the less dense hydrophobic gILs are positioned between the water and the organic phases forming a third one. On the one hand, this is due to the lower density value of the IL under study compared to water, and on the other hand, due to the partial miscibility of diethyl ether with the IL which results in a further reduction of the density. Although there are many examples of solubilization of organic solvents in hydrophobic ILs, most of the hydrophobic ILs are of high density (around 1.4 g cm^{-3}) [15], and the density never is below 1.0 g cm^{-3}. Thus, the behavior in layer sequence shown here is unique for the synthesized relatively "light" gILs and might be of interest in novel reactions or in separation processes or devices.

It has recently been reported that the density of some guanidinium-based RTILs is relatively low compared to the imidazolium series [4b], and that the guanidinium ion is more capable to suppress the effect of the anion than the other cations. In this direction, we found in the present study the same trend in the density behavior, namely, the densities of all of the five series under study are in the range 0.989–1.069 g cm^{-3}, regardless of the anion. Considering the cation, the density decreases as the number of carbon atoms n in the guanidinium ion **C_n-g$^+$** increases, which is typical for RTILs. Thus, the higher the mass of the cation, the lower the density is in a given series (see Table 2). Furthermore, the change of the butyl substituent to decyl in the guanidinium ion leads to a decrease in density for the tertafluoroborate series **C_n-gBF_4** from 1.045 to 0.981 g cm^{-3}, which is rather negligible compared to the methylimidazolium series **C_n-mimBF_4**, with changes from 1.208 to 1.072 for the same substituents. Considering the anion, when the cation is kept constant, the order of density decrease is as follows: $Sac^- > Ace^- > Tos^- > BF_4{}^-$, but just as in the case of the cation, the effect of the anion is negligible, and thus, the densities for the **C_4-g$^+$** series are: 1.063 ≈ 1.050 ≈ 1.027 ≈ 1.009, following the anion sequence considered above. These effects might be attributed to the higher volume (mass respectively) of the guanidinium ion compared to the volume of the counterions. Consequently, it might be concluded that the density of a RTgIL can be determined by using the appropriate guanidinium ion, and at the same time other desirable properties may be varied by simply changing the substituents or counterions. This can be of a great importance for the industrial application of RTILs.

As we mentioned above, the density values of the gILs under study seem to be determined by the molecular volume (mass) of the guanidinium ion. In spite of the negligible differences in density in the separate series, we found this property to be further fine-tunable by using the Residual Volume Approach (RVA), a recently developed method for predicting some physical properties of ILs by using simple correlations between the desired property and newly defined substituent parameters β^X [16, 17]. Plots of $\rho = f(\beta)$ for the synthesized RTgILs are shown in Fig. 2. As can be seen, the density decreases with β^X, and each series follows a very good linear relationship (R^2 = 0.97 – 0.99). The results obtained from Fig. 2 show that the RVA can be applied successfully in the case of guanidinium-based ILs as well, and can be used for predicting the density values of the remaining members of the series by using the empirically obtained linear equation for a given series and the substituent constants β^X [16, 17].

Conclusion

Several series of new homologous N''-n-alkyl-substituted N,N-diethyl-N',N'-di-n-propyl-N''-n-hexyl guanidinium salts with tetrafluoroborate, acesulfamate, saccharinate, and tosylate anions were synthesized and

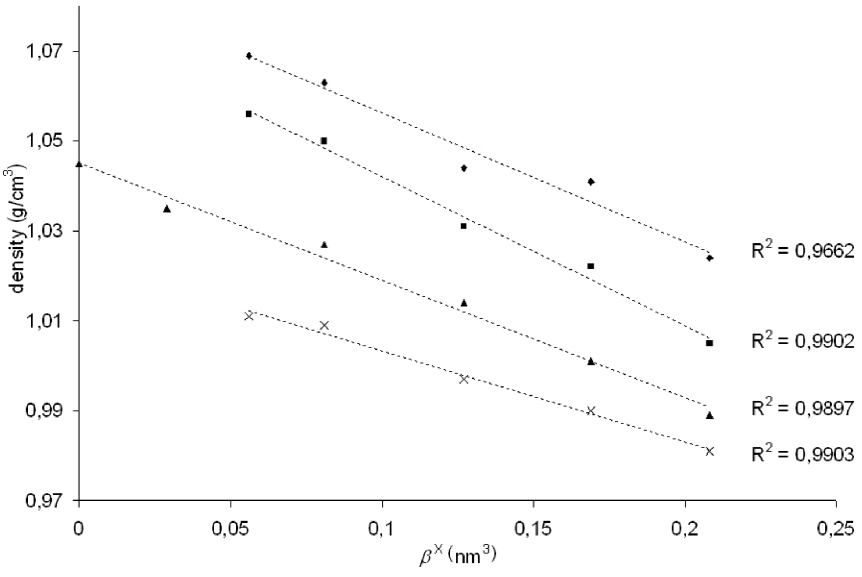


Fig. 2. Residual Volume Approach correlations of densities at 25 °C: ◆ C_n-gSac, ■ C_n-gAce, ▲ C_n-gTos, n = 1, 2, 4, 6, 8, 10 and × C_n-gBF_4, n = 3, 4, 6, 8, 10.

characterized and their physical properties were evaluated. All the salts are hydrophobic liquids at room temperature, allowing an investigation of their water uptake ability and density. The behavior is unique for the synthesized relatively "light" hydrophobic gILs, which might be of interest in novel reactions or in separation processes and devices.

Experimental Section

General remarks

Commercially available reagents were used as supplied. All the other reagents used were dried and freshly distilled prior to use. Distilled water was used for the preparation of aqueous solutions. All glassware was oven-dried at 75 °C before using.

The IR spectra were acquired from thin films on a Perkin-Elmer FT-IR instrument Model Spectrum One and are reported in reciprocal centimeters. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance DRX-250 NMR spectrometer operating at 250.13 and 62.9 Hz, respectively, in the solvent given in parentheses. The chemical shifts are given in ppm (δ) relative to tetramethylsilane as internal standard. Elemental analyses were obtained in the laboratories at the Institute of Organic Chemistry, University of Stuttgart. Prior to their further manipulation (characterization or property measurement), each RTIL was dried under vacuum (0.01 mbar) at 90 °C for at least 6 h.

Water contents

The water content of each RTgIL was determined by Karl-Fischer titration with a Metrohm 831 KF Coulometer.

Density

The reported densities were determined by means of a picnometer (1 cm^3) at 25 °C. The mass of the volume of liquid was taken on an analytical balance and each reported value is the average of two measurements.

Synthesis

N,*N*-diethyl-*N*′,*N*′-di-*n*-propylurea (**1**), *N*,*N*-diethyl-*N*′,*N*′-di-*n*-propylchloroformamidinium chloride (**2**) and the pentasubstituted guanidine **3** were synthesized by protocols published previously by Kantlehner and coworkers [2].

General procedure for the synthesis of guanidinium chlorides ***C$_n$-gCl*** *(n = 3, 4, 6, 8, 10)*

The reactions were carried out in round-bottom flasks equipped with a reflux condenser and a calcium chloride tube. The corresponding alkyl chlorides (3 equiv.) were added to a solution of guanidine **3** in dry DMF, and the reaction mixtures were stirred at 100 – 110 °C (oil bath) for an appropriate time. The consumption of **3** was monitored by FT-IR. After the end of the reaction the volatile ingredients were evaporated under reduced pressure, the residue was dissolved in distilled water and in order to remove any unreacted starting material washed with cyclohexane (6 × 50 cm^3). Afterwards, the main quantity of water was evaporated under reduced pressure (90 °C, 20 mbar), and the residual RTILs **C$_n$-gCl** were further dried at high vacuum (90 °C, 0.01 mbar) for 6 – 8 h. Except **C$_6$-gCl**, which solidified after drying, all the other guanidinium chlorides were obtained as slightly yellow liquids.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-propylguanidinium chloride (**C_3-gCl**)*

This compound was obtained from 43.98 g (0.56 mol) of *n*-propyl chloride and 39.66 g (0.14 mol) of guanidine **3**. – Yield 15.21 g (30 %). – IR (film): ν = 1533 (CN_3^+) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.78 – 1.02 (m, 12 H, 3 × $C_2H_4CH_3$, $C_5H_{10}CH_3$), 1.14 – 1.35 (m, 12 H, 3 × CH_2, 2 × CH_2CH_3), 1.38 – 1.95 (m, 8 H, NCH_2CH_2, 3 × $NCH_2CH_2CH_3$), 2.96 – 3.55 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (2 × CH_3), 11.4 (CH_3), 13.0 (CH_3), 13.1 (CH_3), 13.7 (CH_3), 21.0 (CH_2), 22.5 (3 × CH_2), 26.8 (CH_2), 27.5 (CH_2), 31.1 (CH_2), 44.1 (2 × CH_2N), 49.8 (CH_2N), 51.4 (2 × CH_2N), 51.5 (CH_2N), 163.9 (CN_3^+).

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-butylguanidinium chloride (**C_4-gCl**)*

This compound was obtained from 58.55 cm^3 (51.52 g, 0.56 mol) of *n*-butyl chloride and 39.66 g (0.14 mol) of guanidine **3**. – Yield 44.63 g (89 %). – n_D^{20} = 1.5007. – IR (film): ν = 1532 (CN_3^+) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.80 – 1.03 (m, 12 H, 2 × $C_2H_4CH_3$, $C_3H_6CH_3$, $C_5H_{10}CH_3$), 1.12 – 1.95 (m, 22 H, 8 × CH_2, 2 × CH_2CH_3), 2.92 – 3.56 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 13.1 (CH_3), 13.7 (CH_3), 13.9 (2 × CH_3), 20.1 (CH_2), 21.0 (CH_2), 22.5 (2 × CH_2), 26.6 (CH_2), 27.4 (CH_2), 29.6 (CH_2), 31.3 (CH_2), 44.2 (2 × CH_2N), 49.6 (CH_2N), 49.8 (CH_2N), 51.5 (2 × CH_2N), 163.9 (CN_3^+).

*N,N-Diethyl-N′,N′-di-n-propyl-N″,N″-di-n-hexylguanidinium chloride (**C_6-gCl**)*

This compound was obtained from 21.2 cm^3 (23.88 g, 0.20 mol) of *n*-hexyl chloride and 14.0 g (0.05 mol) of guanidine **3**. – Yield 17.4 g (87 %). – n_D^{20} = 1.4934. – IR (film): ν = 1532 (CN_3^+) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.79 – 1.02 (m, 12 H, 2 × $C_2H_4CH_3$, 2 × $C_5H_{10}CH_3$), 1.16 – 1.95 (m, 26 H, 10 × CH_2, 2 × CH_2CH_3), 2.96 – 3.57 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 13.1 (2 × CH_3), 13.9 (2 × CH_3), 21.0 (CH_2), 21.1 (CH_2), 22.5 (2 × CH_2), 26.5 (CH_2), 26.6 (CH_2), 27.4 (CH_2), 27.6 (CH_2), 31.3 (2 × CH_2), 44.2 (2 × CH_2N), 49.8 (2 × CH_2N), 51.5 (CH_2N), 51.6 (CH_2N), 163.9 (CN_3^+).

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-octylguanidinium chloride (**C_8-gCl**)*

This compound was obtained from 47.5 cm^3 (41.47 g, 0.28 mol) of *n*-octyl chloride and 19.7 g (0.07 mol) of guanidine **3**. – Yield 25.4 g (85 %). – n_D^{20} = 1.4957. – IR (film): ν = 1533 (CN_3^+) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.79 – 1.03 (m, 12 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_7H_{14}CH_3$), 1.11 – 1.90 (m, 30 H, 12 × CH_2, 2 × CH_2CH_3), 2.97 – 3.64 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 13.1 (CH_3), 13.2 (CH_3), 13.9 (CH_3), 14.0 (CH_3), 21.0 (CH_2), 21.1 (CH_2), 22.6 (2 × CH_2), 26.6 (CH_2), 26.9 (CH_2), 27.5 (2 × CH_2), 29.1 (2 × CH_2), 31.3 (CH_2), 31.7 (CH_2), 44.2 (CH_2N), 44.3 (CH_2N), 49.8 (2 × CH_2N), 51.5 (CH_2N), 51.6 (CH_2N), 164.0 (CN_3^+).

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-decylguanidinium chloride (**C_{10}-gCl**)*

This compound was obtained from 38.05 cm^3 (33.11 g, 0.188 mol) of *n*-decyl chloride and 13.28 g (0.047 mol) of guanidine **3**. – Yield 51.4 g (74 %). – n_D^{20} = 1.4935. – IR (film): ν = 1534 (CN_3^+) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.81 – 1.02 (m, 12 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_9H_{18}CH_3$), 1.07 – 1.94 (m, 34 H, 14 × CH_2, 2 × CH_2CH_3), 3.00 – 3.64 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 13.1 (2 × CH_3), 13.9 (CH_3), 14.1 (CH_3), 21.0 (CH_2), 21.1 (CH_2), 22.5 (CH_2), 22.6 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 27.4 (2 × CH_2), 29.2 (2 × CH_2), 29.4 (2 × CH_2), 31.3 (CH_2), 31.8 (CH_2), 44.2 (CH_2N), 44.3 (CH_2N), 49.8 (2 × CH_2N), 51.5 (CH_2N), 51.6 (CH_2N), 163.9 (CN_3^+).

*General procedure for the synthesis of guanidinium p-toluenesulfonates **C_n-gTos** (n = 1, 2, 4, 6, 8, 10)*

In a round-bottom flask equipped with a reflux condenser, the pentasubstituted guanidine **3** was added to a stirred solution of the corresponding tosylate ester in dry DMF. The reaction mixture was then stirred at 110 °C for 2 – 4.30 h. The reaction was monitored by IR spectroscopy. At the end of the reaction the volatile compounds were evaporated on a rotary evaporator, and the residue was washed with diethyl ether (5 × 50 cm^3). The residue was further evaporated first at 90 °C/23 mbar, and than at 0.01 mbar for 8 h.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-methylguanidinium p-toluenesulfonate (**C_1-gTos**)*

This compound was obtained from 11.9 g (0.0639 mol) of methyl tosylate and 16.5 g (0.0581 mol) of guanidine **3** in DMF (110 cm^3). – Yield: 27.02 g (99 %). – n_D^{20} = 1.5145. – IR (film): ν = 1539 (CN_3^+), 1200 (SO_3^-), 677 (Ar) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.75 – 1.02 (m, 9 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$), 1.09 – 1.84 (m, 18 H, 6 × CH_2, 2 × CH_2CH_3), 2.32 (s, 3 H, CH_3–$C_6H_4SO_3^-$), 2.86 – 3.56 (m, 10 H, all CH_2N), 3.03 (d, J = 3.1 Hz, 3 H, NCH_3), 7.10 (d, J = 7.9 Hz, 2 H, $CH_3C_6H_4SO_3^-$), 7.79 (d, J = 8.1 Hz, 2 H, $CH_3C_6H_4SO_3^-$). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.4 (CH_3), 12.7 (CH_3), 12.9 (CH_3), 13.1 (CH_3), 13.9

(CH_3), 20.8 (CH_2), 21.0 (CH_2), 21.3 (CH_3), 22.5 (CH_2), 26.5 (CH_2), 27.2 (CH_2), 31.3 (CH_2), 38.6 and 38.9 (CH_3N-rotamers), 43.3 (CH_2N), 43.7 (CH_2N), 44.0 (CH_2N), 51.3 (CH_2N), 52.9 (CH_2N), 126.1 (2 × –CH=), 128.3 (2 × –CH=), 138.5 (C-CH_3), 144.5 (C-SO_3), 164.0 (CN_3^+). – Anal. for $C_{25}H_{47}N_3O_3S$ (469.7) × H_2O: calcd. C 61.56, H 10.13, N 8.62; found C 61.55, H 9.95, N 8.53.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-ethylguanidinium p-toluenesulfonate (**C_2-gTos**)*

This compound was obtained from 8.58 g (0.0428 mol) of ethyl tosylate and 11.04 g (0.0390 mol) of guanidine **3** in DMF (80 cm^3). – Yield: 17.7 g (94 %). – n_D^{20} = 1.5136. – IR (film): ν = 1535 (CN_3^+), 1201 (SO_3^-), 678 (Ar). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.74 – 1.02 (m, 9 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$), 1.05 – 1.88 (m, 21 H, 6 × CH_2, 3 × CH_2CH_3), 2.32 (s, 3 H, CH_3–$C_6H_4SO_3^-$), 2.87 – 3.56 (m, 12 H, all CH_2N), 7.10 (d, J = 7.9 Hz, 2 H, $CH_3C_6H_4SO_3^-$), 7.81 (d, J = 8.1 Hz, 2 H, $CH_3C_6H_4SO_3^-$). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.4 (CH_3), 12.9 (2 × CH_3), 13.0 (2 × CH_3), 13.9 (CH_3), 20.9 (CH_2), 21.3 (CH_3), 22.5 (CH_2), 26.6 (CH_2), 27.3 (CH_2), 27.4 (CH_2), 31.3 (CH_2), 44.0 (CH_2N), 44.1 (CH_2N), 44.6 (CH_2N), 49.0 (CH_2N), 51.3 (CH_2N), 51.4 (CH_2N), 126.2 (2 × –CH=), 128.2 (2 × –CH=), 138.4 (C-CH_3), 144.7 (C-SO_3), 163.8 (CN_3^+). – Anal. for $C_{26}H_{49}N_3O_3S$ (483.8) × H_2O: calcd. C 62.24, H 10.24, N 8.37; found C 62.65, H 9.86, N 8.58.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-butylguanidinium p-toluenesulfonate (**C_4-gTos**)*

This compound was obtained from 12.17 g (0.0533 mol) of *n*-butyl tosylate and 13.74 g (0.0485 mol) of guanidine **3** in DMF (100 cm^3). – Yield: 22.1 g (89 %). – n_D^{20} = 1.5123. – IR (film): ν = 1535 (CN_3^+), 1202 (SO_3^-), 677 (Ar). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.74 – 1.02 (m, 12 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_3H_7CH_3$), 1.05 – 1.88 (m, 22 H, 8 × CH_2, 2 × CH_2CH_3), 2.32 (s, 3 H, CH_3–$C_6H_4SO_3^-$), 2.87 – 3.56 (m, 12 H, all CH_2N), 7.10 (d, J = 7.9 Hz, 2 H, $CH_3C_6H_4SO_3^-$), 7.81 (d, J = 8.1 Hz, 2 H, $CH_3C_6H_4SO_3^-$). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.2 (CH_3), 11.4 (CH_3), 12.9 (2 × CH_3), 13.7 (CH_3), 13.9 (CH_3), 20.0 (CH_2), 20.9 (CH_2), 21.0 (CH_2), 21.3 (CH_3), 22.5 (CH_2), 26.6 (CH_2), 27.4 (CH_2), 29.5 (CH_2), 31.3 (CH_2), 44.0 (CH_2N), 44.1 (CH_2N), 49.6 (CH_2N), 49.7 (CH_2N), 51.3 (CH_2N), 51.4 (CH_2N), 126.2 (2 × –CH=), 128.2 (2 × –CH=), 138.4 (C-CH_3), 144.7 (C-SO_3), 163.8 (CN_3^+). – Anal. for $C_{28}H_{53}N_3O_3S$ (511.8) × H_2O: calcd. C 63.47, H 10.46, N 7.93; found C 63.55, H 10.11, N 8.39.

*N,N-Diethyl-N′,N′-di-n-propyl-N″,N″-di-n-hexylguanidinium p-toluenesulfonate (**C_6-gTos**)*

This compound was obtained from 12.09 g (0.0472 mol) of *n*-hexyl tosylate and 12.15 g (0.0429 mol) of guanidine **3** in DMF (95 cm^3). – Yield: 20.36 g (88 %). – n_D^{20} = 1.508. – IR (film): ν = 1535 (CN_3^+), 1202 (SO_3^-), 677 (Ar). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.74 – 1.01 (m, 12 H, 2 × $C_2H_4CH_3$, 2 × $C_5H_{10}CH_3$), 1.04 – 1.94 (m, 26 H, 10 × CH_2, 2 × CH_2CH_3), 2.32 (s, 3 H, CH_3–$C_6H_4SO_3^-$), 2.90 – 3.57 (m, 12 H, all CH_2N), 7.11 (d, J = 7.9 Hz, 2 H, $CH_3C_6H_4SO_3^-$), 7.82 (d, J = 8.1 Hz, 2 H, $CH_3C_6H_4SO_3^-$). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 12.9 (CH_3), 13.0 (CH_3), 13.9 (CH_3), 14.0 (CH_3), 20.9 (CH_2), 21.0 (CH_2), 21.3 (CH_3), 22.5 (2 × CH_2), 26.5 (CH_2), 26.7 (CH_2), 27.4 (CH_2), 27.5 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 44.0 (CH_2N), 44.2 (CH_2N), 49.6 (2 × CH_2N), 51.3 (CH_2N), 51.5 (CH_2N), 126.2 (2 × –CH=), 128.3 (2 × –CH=), 138.4 (C-CH_3), 144.5 (C-SO_3), 164.0 (CN_3^+). – Anal. for $C_{30}H_{57}N_3O_3S$ (539.9) × H_2O: calcd. C 64.59, H 10.66, N 7.53; found C 64.38, H 10.11, N 7.93.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-octylguanidinium p-toluenesulfonate (**C_8-gTos**)*

This compound was obtained from 9.78 g (0.0344 mol) of *n*-octyl tosylate and 8.86 g (0.0313 mol) of guanidine **3** in DMF (80 cm^3). – Yield: 16.20 g (83 %). – n_D^{20} = 1.5034. – IR (film): ν = 1534 (CN_3^+), 1202 (SO_3^-), 677 (Ar). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.77 – 1.00 (m, 12 H, 2 × $C_2H_4CH_3$, $C_7H_{14}CH_3$, $C_5H_{10}CH_3$), 1.04 – 1.91 (m, 30 H, 12 × CH_2, 2 × CH_2CH_3), 2.32 (s, 3 H, CH_3–$C_6H_4SO_3^-$), 2.85 – 3.51 (m, 12 H, all CH_2N), 7.10 (d, J = 7.9 Hz, 2 H, $CH_3C_6H_4SO_3^-$), 7.82 (d, J = 8.1 Hz, 2 H, $CH_3C_6H_4SO_3^-$). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 12.9 (CH_3), 13.0 (CH_3), 13.9 (CH_3), 14.1 (CH_3), 20.9 (CH_2), 21.0 (CH_2), 21.2 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 26.5 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 26.9 (CH_2), 27.4 (CH_2), 29.1 (CH_2), 31.3 (CH_2), 31.7 (CH_2), 44.0 (CH_2N), 44.1 (CH_2N), 49.7 (2 × CH_2N), 51.4 (CH_2N), 51.5 (CH_2N), 126.2 (2 × –CH=), 128.2 (2 × –CH=), 138.3 (C-CH_3), 144.8 (C-SO_3), 163.9 (CN_3^+). – Anal. for $C_{32}H_{61}N_3O_3S$ (567.9) × 0.5 H_2O: calcd. C 66.62, H 10.83, N 7.28; found C 66.10, H 10.49, N 7.74.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-decylguanidinium p-toluenesulfonate (**C_{10}-gTos**)*

This compound was obtained from 12.62 g (0.0468 mol) of *n*-decyl tosylate and 12.06 g (0.0425 mol) of guanidine **3** in DMF (100 cm^3). – Yield: 23.58 g (93 %). – n_D^{20} = 1.5007. – IR (film): ν = 1535 (CN_3^+), 1202 (SO_3^-), 678 (Ar). – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.77 – 1.00 (m, 12 H, 2 × $C_2H_4CH_3$, $C_9H_{18}CH_3$, $C_5H_{10}CH_3$), 1.07 – 1.92 (m, 34 H, 14 × CH_2, 2 × CH_2CH_3), 2.31 (s, 3 H, CH_3–$C_6H_4SO_3^-$), 2.88 – 3.52 (m, 12 H, all CH_2N), 7.09 (d, J = 7.1 Hz, 2 H, $CH_3C_6H_4SO_3^-$), 7.82 (d, J = 8.1 Hz, 2 H, $CH_3C_6H_4SO_3^-$). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 12.9 (CH_3), 13.0 (CH_3), 13.9 (CH_3), 14.1 (CH_3), 20.9 (CH_2), 21.0 (CH_2), 21.3 (CH_3),

22.5 (CH_2), 22.6 (CH_2), 26.5 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 26.9 (CH_2), 27.4 (CH_2), 27.5 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 44.0 (CH_2N), 44.1 (CH_2N), 50.0 (2 × CH_2N), 51.4 (CH_2N), 51.5 (CH_2N), 126.2 (2 × –CH=), 128.2 (2 × –CH=), 138.1 (C-CH_3), 145.0 (C-SO_3), 163.9 (CN_3^+). – Anal. for $C_{34}H_{65}N_3O_3S$ (596.0) × 0.5 H_2O: calcd. C 67.50, H 11.00, N 6.95; found C 67.51, H 10.87, N 6.82.

General procedure for anion metathesis reactions. Synthesis of guanidinium tetrafluoroborates ***C_n-gBF$_4$****, acesulfamates* ***C_n-gAce****, and saccharinates* ***C_n-gSac*** *(n = 3, 4, 6, 8, 10)*

Metathesis reaction in methanol

A methanol solution of the RTIL **C_n-gCl** was slowly added dropwise to a stirred suspension of sodium tetrafluoroborate in methanol at 60 °C. The flask was equipped with a magnetic stirrer, a dropping funnel, a reflux condenser and a calcium chloride tube. The reaction mixture was stirred for 4 h at reflux and cooled to r. t., and the formed white precipitate of sodium chloride was removed by filtration. The filtrate was distilled under reduced pressure giving the crude product of the metathesis reaction. In order to remove the residual sodium chloride, the residue was dissolved in a small quantity of dry THF, filtered, and the solvent was evaporated on a rotary evaporator. The residue was further dissolved in a small quantity of dichloromethane and washed with distilled water until the probe for chloride anions ($AgNO_3$ test) was negative. The dichloromethane layer was dried with sodium sulfate and filtered, and dichloromethane was evaporated on a rotary evaporator. The resulting slight yellow RTILs **C_n-gBF$_4$** were further dried *in vacuo* (90 °C/0.01 mbar) for 6 – 8 h.

Metathesis reaction in water

A solution of the RTIL **C_n-gCl** in water was slowly added dropwise to a saturated stirred solution of the corresponding sodium or potassium salt in water at 60 °C. The flask was equipped with a magnetic stirrer, a dropping funnel, a reflux condenser, and a calcium chloride tube. The reaction mixture was stirred for 4 h at 60 °C and then left to cool over night. The resulting two layers were separated, and the product of the metathesis reaction (the top layer) was dissolved in dichloromethane and washed with water until the probe for chloride anions ($AgNO_3$ test) was negative. The dichloromethane layer was dried with sodium sulfate and filtered, and dichloromethane was evaporated on a rotary evaporator. The resulting slightly yellow RTILs **C_n-gX** were further dried *in vacuo* (90 °C/0.01 mbar) for 6 – 8 h.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-propylguanidinium tetrafluoroborate (**C_3-gBF$_4$**)*

This compound was obtained from 7.02 g (0.019 mol) of **C_3-gCl** in CH_3OH (45 cm^3) and 2.52 g (0.023 mol) of $NaBF_4$ in CH_3OH (25 cm^3). – Yield 7.7 g (98 %). – n_D^{20} = 1.4578. – IR (film): ν = 1534 (CN_3^+), 1034 and 1047 (B–F) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.83 – 1.01 (m, 12 H, 3 × $C_2H_4CH_3$, $C_5H_{10}CH_3$), 1.15 – 1.89 (m, 20 H, 7 × CH_2, 2 × CH_2CH_3), 2.93 – 3.49 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.2 (2 × CH_3), 11.3 (CH_3), 12.7 (CH_3), 13.9 (2 × CH_3), 20.8 (CH_2), 22.5 (3 × CH_2), 26.5 (CH_2), 27.4 (CH_2), 31.3 (CH_2), 43.8 (2 × CH_2N), 49.6 (CH_2N), 51.3 (3 × CH_2N), 164.1 (s, CN_3^+). – Anal. for $C_{20}H_{44}BF_4N_3$ (413.4): calcd. C 58.11, H 10.73, N 10.16; found C 57.52, H 10.49, N 10.29.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-butylguanidinium tetrafluoroborate (**C_4-gBF$_4$**)*

This compound was obtained from 9.16 g (0.025 mol) of **C_4-gCl** in CH_3OH (60 cm^3) and 3.18 g (0.03 mol) of $NaBF_4$ in CH_3OH (30 cm^3). – Yield 10.2 g (96 %). – n_D^{20} = 1.4572. – IR (film): ν = 1534 (CN_3^+), 1033 and 1048 (B–F) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.81 – 1.02 (m, 12 H, 2 × $C_2H_4CH_3$, $C_3H_6CH_3$, $C_5H_{10}CH_3$), 1.14 – 1.90 (m, 22 H, 8 × CH_2, 2× CH_2CH_3), 2.92 – 3.51 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (2 × CH_3), 12.8 (CH_3), 12.9 (CH_3), 13.9 (2 × CH_3), 20.1 (CH_2), 20.8 (CH_2), 22.5 (2 × CH_2), 26.6 (CH_2), 27.4 (CH_2), 29.5 (CH_2), 31.3 (CH_2), 43.8 (2 × CH_2N), 49.4 (CH_2N), 49.6 (CH_2N), 51.4 (2 × CH_2N), 164.0 (CN_3^+). – Anal. for $C_{21}H_{46}BF_4N_3$ (427.4) × H_2O: calcd. C 57.79, H 10.85, N 9.63; found C 58.19, H 10.62, N 10.07.

*N,N-Diethyl-N′,N′-di-n-propyl-N″,N″-di-n-hexylguanidinium tetrafluoroborate (**C_6-gBF$_4$**)*

This compound was obtained from 12.59 g (0.031 mol) of **C_6-gCl** in CH_3OH (80 cm^3) and 4.1 g (0.037 mol) of $NaBF_4$ in CH_3OH (40 cm^3). – Yield 13.4 g (94 %). – n_D^{20} = 1.4597. – IR (film): ν = 1533 (CN_3^+), 1033 and 1047 (B–F) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.81 – 1.01 (m, 12 H, 2 × $C_2H_4CH_3$, 2 × $C_5H_{10}CH_3$), 1.15 – 1.89 (m, 26 H, 10 × CH_2, 2 × CH_2CH_3), 2.91 – 3.53 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.2 (CH_3), 11.3 (CH_3), 12.7 (CH_3), 12.8 (CH_3), 13.9 (2 × CH_3), 20.8 (CH_2), 20.9 (CH_2), 22.5 (2 × CH_2), 26.5 (CH_2), 26.6 (CH_2), 27.3 (CH_2), 27.4 (CH_2), 31.3 (2 × CH_2), 43.8 (CH_2N), 43.9 (CH_2N), 49.7 (2 × CH_2N), 51.3 (CH_2N), 51.4 (CH_2N), 164.0 (CN_3^+). – Anal. for $C_{23}H_{50}BF_4N_3$ (455.5): calcd. C 60.65, H 11.06, N 9.23; found C 60.48, H 10.91, N 9.16.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-octylguanidinium tetrafluoroborate (**C_8-gBF$_4$**)*

This compound was obtained from 17.9 g (0.041 mol) of **C_8-gCl** in CH_3OH (110 cm^3) and 5.45 g (0.049 mol)

$NaBF_4$ in CH_3OH (55 cm^3). – Yield = 19.6 g (98 %). – n_D^{20} = 1.4580. – IR (film): ν = 1534 (CN_3^+), 1034 and 1048 (B–F) cm^{-1}. – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.79 – 0.99 (m, 12 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_7H_{14}CH_3$), 1.17 – 1.84 (m, 30 H, 12 × CH_2, 2 × CH_2CH_3), 2.93 – 3.52 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (2 × CH_3), 12.7 (CH_3), 12.8 (CH_3), 14.0 (2 × CH_3), 20.8 (CH_2), 20.9 (CH_2), 22.5 (CH_2), 22.6 (CH_2), 26.5 (CH_2), 27.4 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 30.3 (2 × CH_2), 31.3 (CH_2), 31.7 (CH_2), 43.8 (2 × CH_2N), 43.9 (CH_2N), 49.6 (CH_2N), 51.4 (2 × CH_2N), 164.0 (CN_3^+). – Anal. for $C_{25}H_{54}BF_4N_3$ (483.5) × 0.5 H_2O: calcd. C 60.96, H 11.26, N 8.53; found C 61.00, H 11.11, N 9.11.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-decylguanidinium tetrafluoroborate (**C_{10}-gBF$_4$**)*

This compound was obtained from 18.00 g (0.039 mol) of **C_{10}-gCl** in CH_3OH (115 cm^3) and 5.15 g (0.047 mol) $NaBF_4$ in CH_3OH (52 cm^3). – Yield = 19.4 g (97 %). – n_D^{20} = 1.4567. – IR (film): ν = 1535 (CN_3^+), 1034 and 1048 (B–F) cm^{-1}. – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.79 – 1.01 (m, 12 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_9H_{18}CH_3$), 1.13 – 1.91 (m, 34 H, 14 × CH_2, 2 × CH_2CH_3), 2.94 – 3.51 (m, 12 H, all CH_2N). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.2 (CH_3), 11.3 (CH_3), 12.7 (CH_3), 12.8 (CH_3), 14.0 (CH_3), 14.1 (CH_3), 20.8 (CH_2), 20.9 (CH_2), 22.5 (CH_2), 22.6 (CH_2), 26.5 (CH_2), 27.3 (CH_2), 27.4 (2 × CH_2), 29.2 (2 × CH_2), 29.5 (2 × CH_2), 31.3 (CH_2), 31.8 (CH_2), 43.9 (2 × CH_2N), 49.6 (CH_2N), 49.7 (CH_2N), 51.3 (2 × CH_2N), 164.0 (CN_3^+). – Anal. for $C_{27}H_{58}BF_4N_3$ (511.6) × 0.5 H_2O: calcd. C 62.29, H 11.42, N 8.07; found C 62.00, H 11.33, N, 8.67.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-propylguanidinium acesulfamate (**C_3-gAce**)*

This compound was obtained from 7.18 g (0.021 mol) of **C_3-gCl** in CH_3OH (4.14 cm^3) and 8.25 g (0.041 mol) acesulfame-K in CH_3OH (8 cm^3). – Yield = 9.2 g (92 %). – n_D^{20} = 1.5032. – IR (film): ν = 1533 (CN_3^+), 1171 (SO_2), 1602 (C=C), 1650 (C=O) cm^{-1}. – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.80 – 1.01 (m, 12 H, 3 × $C_2H_4CH_3$, $C_5H_{10}CH_3$), 1.17 – 1.91 (m, 20 H, 7 × CH_2, 2 × CH_2CH_3), 2.00 (d, J = 1.0 Hz, 3H, CH_3/Ace), 2.95 – 3.50 (m, 12 H, all CH_2N), 5.46 (d, J = 1.0 Hz, 1 H, CH/Ace). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 12.8 (CH_3), 12.9 (CH_3), 13.9 (2 × CH_3), 19.9 (CH_3/Ace), 20.9 (CH_2), 22.5 (3 × CH_2), 26.6 (CH_2), 27.5 (CH_2), 31.3 (CH_2), 44.0 (CH_2N), 44.1 (CH_2N), 49.7 (CH_2N), 51.4 (3 × CH_2N), 102.4 (CH/Ace), 160.3 (C–O/Ace), 163.9 (CN_3^+), 169.8 (C=O/Ace). – Anal. for $C_{24}H_{48}N_4O_4S$ (488.7) × H_2O: calcd. C 56.88, H 9.95, N 11.06; found C 57.70, H 9.89, N 11.39.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-butylguanidinium acesulfamate (**C_4-gAce**)*

This compound was obtained from 20.58 g (0.056 mol) of **C_4-gCl** in H_2O and 57.05 g (0.284 mol) acesulfame-K in H_2O. – Yield = 26.2 g (92 %). – n_D^{20} = 1.5019. – IR (film): ν = 1534 (CN_3^+), 1172 (SO_2), 1602 (C=C), 1650 (C=O) cm^{-1}. – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.86 – 1.01 (m, 12 H, 2 × $C_2H_4CH_3$, $C_3H_6CH_3$, $C_5H_{10}CH_3$), 1.12 – 1.90 (m, 22 H, 8 × CH_2, 2 × CH_2CH_3), 1.99 (d, J = 1.0 Hz, 3 H, CH_3/Ace), 2.95 – 3.51 (m, 12 H, all CH_2N), 5.46 (d, J = 1.0 Hz, 1 H, CH/Ace). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 12.9 (CH_3), 13.7 (CH_3), 13.9 (2 × CH_3), 20.1 (CH_3/Ace), 20.9 (CH_2), 21.0 (CH_2), 22.5 (2 × CH_2), 26.6 (CH_2), 27.4 (CH_2), 29.5 (CH_2), 31.3 (CH_2), 44.0 (2 × CH_2N), 49.4 (CH_2N), 49.7 (CH_2N), 51.4 (2 × CH_2N), 102.3 (CH/Ace), 160.3 (C–O/Ace), 163.9 (CN_3^+), 169.7 (C=O/Ace). – Anal. for $C_{25}H_{50}N_4O_4S$ (502.8) × 0.5 H_2O: calcd. C 58.67, H 10.04, N 10.95; found C 58.35, H 9.88, N 11.19.

*N,N-Diethyl-N′,N′-di-n-propyl-N″,N″-di-n-hexylguanidinium acesulfamate (**C_6-gAce**)*

This compound was obtained from 22.84 g (0.0565 mol) of **C_6-gCl** in H_2O and 22.74 g (0.113 mol) acesulfame-K in H_2O. – Yield = 26.5 g (88 %). – n_D^{20} = 1.4994. – IR (film): ν = 1532 (CN_3^+), 1172 (SO_2), 1603 (C=C), 1650 (C=O) cm^{-1}. – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.86 – 0.97 (m, 12 H, 2 × $C_2H_4CH_3$, 2 × $C_5H_{10}CH_3$), 1.13 – 1.89 (m, 26 H, 10 × CH_2, 2 × CH_2CH_3), 1.99 (d, J = 1.0 Hz, 3 H, CH_3/Ace), 2.94 – 3.51 (m, 12 H, all CH_2N), 5.48 (d, J = 1.0 Hz, 1 H, CH/Ace). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 12.9 (2× CH_3), 13.9 (2× CH_3), 20.0 (CH_3/Ace), 21.0 (2× CH_2), 22.5 (2× CH_2), 26.5 (2× CH_2), 27.4 (2× CH_2), 31.3 (2× CH_2), 44.1 (2× CH_2N), 49.7 (2× CH_2N), 51.4 (2× CH_2N), 102.3 (CH/Ace), 160.3 (C–O/Ace), 163.9 (s, CN_3^+), 169.7 (C=O/Ace). – Anal. for $C_{27}H_{54}N_4O_4S$ (530.8) × H_2O: calcd. C 59.09, H 10.28, N 10.21; found C 59.47, H 10.16, N 10.25.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-octylguanidinium acesulfamate (**C_8-gAce**)*

This compound was obtained from 12.37 g (0.028 mol) of **C_8-gCl** in H_2O and 28.8 g (0.143 mol) acesulfame-K in H_2O. – Yield = 15.9 g (99 %). – n_D^{20} = 1.4978. – IR (film): ν = 1533 (CN_3^+), 1172 (SO_2), 1601 (C=C), 1650 (C=O) cm^{-1}. – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.77 – 1.01 (m, 12 H, 2× $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_7H_{14}CH_3$), 1.08 – 1.91 (m, 30 H, 12 × CH_2, 2 × CH_2CH_3), 1.99 (d, J = 1.0 Hz, 3 H, CH_3/Ace), 3.00 – 3.52 (m, 12 H, all CH_2N), 5.46 (d, J = 1.0 Hz, 1 H, CH/Ace). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.4 (2× CH_3), 12.9 (CH_3), 13.0 (CH_3), 13.9 (CH_3), 14.1 (CH_3), 19.9 (CH_3/Ace), 20.9 (CH_2), 21.0 (CH_2), 22.5 (CH_2), 22.6 (CH_2), 26.6 (CH_2), 26.9 (CH_2), 27.5 (2×

CH_2), 29.2 (2× CH_2), 31.3 (CH_2), 31.7 (CH_2), 44.0 (CH_2N), 44.1 (CH_2N), 49.7 (2× CH_2N), 51.4 (CH_2N), 51.5 (CH_2N), 102.3 (CH/Ace), 160.4 (C–O/Ace), 163.9 (CN_3^+), 169.8 (C=O/Ace). – Anal. for $C_{29}H_{58}N_4O_4S$ (558.9) × H_2O: calcd. C 60.38, H 10.48, N 9.71; found C 60.38, H 10.27, N 9.89.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-decylguanidinium acesulfamate (**C_{10}-gAce**)*

This compound was obtained from 15.62 g (0.034 mol) of **C_{10}-gCl** in H_2O and 34.21 g (0.17 mol) of acesulfame-K in H_2O. – Yield = 19.4 g (97 %). – n_D^{20} = 1.4952. – IR (film): ν = 1533 (CN_3^+), 1172 (SO_2), 1603 (C=C), 1650 (C=O) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.79 – 1.01 (m, 12 H, 2× $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_9H_{18}CH_3$), 1.12 – 1.89 (m, 34 H, 14 × CH_2, 2 × CH_2CH_3), 2.00 (d, J = 1.0 Hz, 3 H, CH_3/Ace), 2.88 – 3.53 (m, 12 H, all CH_2N), 5.46 (d, J = 1.0 Hz, 1 H, CH/Ace). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 12.9 (2× CH_3), 13.9 (CH_3), 14.1 (CH_3), 19.9 (CH_3/Ace), 20.9 (CH_2), 22.6 (CH_2), 26.5 (CH_2), 26.6 (CH_2), 26.9 (2× CH_2), 27.4 (CH_2), 27.5 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (2× CH_2), 31.3 (CH_2), 31.8 (CH_2), 43.9 (CH_2N), 44.0 (CH_2N), 49.7 (2× CH_2N), 51.4 (2× CH_2N), 102.4 (CH/Ace), 160.4 (C–O/Ace), 163.9 (CN_3^+), 169.8 (C=O/Ace). – Anal. for $C_{31}H_{62}N_4O_4S$ (586.9): calcd. C 61.55, H 10.66, N 9.26; found C 61.60, H 10.55, N 9.24.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-propylguanidinium saccharinate (**C_3-gSac**)*

This compound was obtained from 8.86 g (0.025 mol) of **C_3-gCl** in H_2O and 30.6 g (0.127 mol) of sodium saccharinate in H_2O. – Yield = 10.3 g (82 %). – n_D^{20} = 1.5304. – IR (film): ν = 1534 (CN_3^+), 1116 and 1142 (SO_2), 1583 (C=C), 1637 (C=O) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.78 – 0.98 (m, 12 H, 3× $C_2H_4CH_3$, $C_5H_{10}CH_3$), 1.09 – 1.90 (m, 20 H, 7 × CH_2, 2 × CH_2CH_3), 2.89 – 3.55 (m, 12 H, all CH_2N), 7.46 – 7.53 (m, 2 H, 2 × CH/Sac), 7.66 – 7.75 (m, 1 H, CH/Sac), 7.76 – 7.83 (m, 1 H, CH/Sac). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (3 × CH_3), 12.9 (CH_3), 13.9 (2 × CH_3), 20.9 (CH_2), 22.5 (3 × CH_2), 26.6 (CH_2), 27.4 (CH_2), 31.3 (CH_2), 44.0 (2 × CH_2N), 49.6 (CH_2N), 51.3 (3 × CH_2N), 119.4 (CH/Sac), 123.1 (CH/Sac), 130.6 (CH/Sac), 131.3 (CH/Sac), 135.4 (C/Sac), 145.3 (C–S/Sac), 163.9 (CN_3^+), 170.0 (C=O/Sac). – Anal. for $C_{27}H_{48}N_4O_3S$ (508.8) × 0.5 H_2O: calcd. C 62.88, H 9.54, N 10.82; found C 62.43, H 9.38, N 11.03.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-butylguanidinium saccharinate (**C_4-gSac**)*

This compound was obtained from 14.2 g (0.039 mol) of **C_4-gCl** in H_2O and 47.3 g (0.196 mol) of sodium saccharinate in H_2O. – Yield = 19.0 g (95 %). – n_D^{20} = 1.5274. – IR (film): ν = 1533 (CN_3^+), 1116 and 1142 (SO_2), 1583 (C=C), 1637 (C=O) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.77 – 0.99 (m, 12 H, 2× $C_2H_4CH_3$, $C_3H_6CH_3$, $C_5H_{10}CH_3$), 1.09 – 1.91 (m, 22 H, 8 × CH_2, 2 × CH_2CH_3), 2.93 – 3.55 (m, 12 H, all CH_2N), 7.45 – 7.54 (m, 2 H, 2 × CH/Sac), 7.69 – 7.76 (m, 1 H, CH/Sac), 7.77 – 7.83 (m, 1 H, CH/Sac). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 12.9 (CH_3), 13.7 (CH_3), 13.9 (CH_3), 14.0 (CH_3), 20.1 (CH_2), 20.9 (CH_2), 22.5 (2 × CH_2), 26.6 (CH_2), 27.4 (CH_2), 29.4 (CH_2), 31.3 (CH_2), 44.0 (CH_2N), 44.1 (CH_2N), 49.7 (CH_2N), 50.9 (CH_2N), 51.3 (CH_2N), 52.4 (CH_2N), 119.5 (CH/Sac), 123.1 (CH/Sac), 130.7 (CH/Sac), 131.6 (CH/Sac), 135.3 (C/Sac), 145.2 (C–S/Sac), 164.0 (CN_3^+), 169.9 (C=O/Sac). – Anal. for $C_{28}H_{50}N_4O_3S$ (522.8) × H_2O: calcd. C 62.19, H 9.69, N 10.36; found C 62.48, H 9.42, N 10.88.

*N,N-Diethyl-N′,N′-di-n-propyl-N″,N″-di-n-hexylguanidinium saccharinate (**C_6-gSac**)*

This compound was obtained from 7.35 g (0.018 mol) of **C_6-gCl** in H_2O and 22.0 g (0.091 mol) of sodium saccharinate in H_2O. – Yield = 9.4 g (94 %). – n_D^{20} = 1.5211. – IR (film): ν = 1532 (CN_3^+), 1116 and 1143 (SO_2), 1583 (C=C), 1637 (C=O) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.79 – 1.00 (m, 12 H, 2 × $C_2H_4CH_3$, 2 × $C_5H_{10}CH_3$), 1.14 – 1.88 (m, 26 H, 10 × CH_2, 2 × CH_2CH_3), 2.93 – 3.54 (m, 12 H, all CH_2N), 7.44 – 7.51 (m, 2 H, 2 × CH/Sac), 7.68 – 7.74 (m, 1 H, CH/Sac), 7.77 – 7.83 (m, 1 H, CH/Sac). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 13.0 (2 × CH_3), 13.9 (2 × CH_3), 20.9 (CH_2), 21.0 (CH_2), 22.5 (2 × CH_2), 26.5 (CH_2), 26.6 (CH_2), 27.4 (CH_2), 27.5 (CH_2), 31.3 (2 × CH_2), 44.0 (CH_2N), 44.1 (CH_2N), 49.7 (2 × CH_2N), 51.4 (CH_2N), 51.5 (CH_2N), 119.4 (CH/Sac), 123.1 (CH/Sac), 130.5 (CH/Sac), 131.2 (CH/Sac), 135.6 (C/Sac), 145.4 (C–S/Sac), 164.0 (CN_3^+), 169.9 (C=O/Sac). – Anal. for $C_{30}H_{54}N_4O_3S$ (550.8): calcd. C 65.41, H 9.88, N 10.17; found C 65.22, H 9.85, N 10.13.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N″-n-octylguanidinium saccharinate (**C_8-gSac**)*

This compound was obtained from 14.9 g (0.034 mol) of **C_8-gCl** in H_2O and 41.7 g (0.173 mol) of sodium saccharinate in H_2O. – Yield = 19.8 g (99 %). – n_D^{20} = 1.5202. – IR (film): ν = 1533 (CN_3^+), 1116 and 1143 (SO_2), 1583 (C=C), 1637 (C=O) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.77 – 1.00 (m, 12 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_7H_{14}CH_3$), 1.09 – 1.91 (m, 30 H, 12 × CH_2, 2 × CH_2CH_3), 2.88 – 3.57 (m, 12 H, all CH_2N), 7.46 – 7.53 (m, 2 H, 2 × CH/Sac), 7.68 – 7.75 (m, 1 H, CH/Sac), 7.76 – 7.84 (m, 1 H, CH/Sac). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (2 × CH_3), 12.9 (2 × CH_3), 13.9 (CH_3), 14.1 (CH_3), 20.9 (CH_2), 21.0 (CH_2), 22.6 (2 × CH_2), 26.6 (CH_2), 26.8 (CH_2), 27.4

(2 × CH_2), 29.1 (2 × CH_2), 31.2 (CH_2), 31.7 (CH_2), 44.0 (2 × CH_2N), 49.7 (2 × CH_2N), 51.3 (CH_2N), 51.4 (CH_2N), 119.4 (CH/Sac), 123.1 (CH/Sac), 130.6 (CH/Sac), 131.3 (CH/Sac), 135.3 (C/Sac), 145.3 (C–S/Sac), 163.9 (CN_3^+), 169.8 (C=O/Sac). – Anal. for $C_{32}H_{58}N_4O_3S$ (578.9) × 1.5 H_2O: calcd. C 63.43, H 10.15, N 9.25; found C 63.20, H 9.83, N 9.30.

*N,N-Diethyl-N′,N′-di-n-propyl-N″-n-hexyl-N‴-n-decylguanidinium saccharinate (**C_{10}-gSac**)*

This compound was obtained from 7.58 g (0.016 mol) of **C_{10}-gCl** in H_2O and 19.9 g (0.082 mol) of sodium saccharinate in H_2O. – Yield = 9.9 g (99 %). – n_D^{20} = 1.5184. – IR (film): ν = 1533 (CN_3^+), 1116 and 1143 (SO_2), 1583 (C=C), 1637 (C=O) cm^{-1}. – ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.78 – 0.98 (m, 12 H, 2 × $C_2H_4CH_3$, $C_5H_{10}CH_3$, $C_9H_{18}CH_3$), 1.11 – 1.91 (m, 34 H, 14 × CH_2, 2 × CH_2CH_3), 2.91 – 3.56 (m, 12 H, all CH_2N), 7.45 – 7.53 (m, 2 H, 2 × *CH*/Sac), 7.69 – 7.75 (m, 1 H, *CH*/Sac), 7.76 – 7.83 (m, 1 H, *CH*/Sac). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.3 (CH_3), 11.4 (CH_3), 13.0 (CH_3), 13.9 (CH_3), 14.1 (2 × CH_3), 20.9 (CH_2), 21.0 (CH_2), 22.5 (CH_2), 22.6 (CH_2), 26.6 (CH_2), 26.9 (CH_2), 27.4 (2 × CH_2), 29.3 (2 × CH_2), 29.5 (2 × CH_2), 31.3 (CH_2), 31.8 (CH_2), 44.0 (CH_2N), 44.2 (CH_2N), 49.7 (2 × CH_2N), 51.4 (CH_2N), 51.5 (CH_2N), 119.5 (CH/Sac), 123.1 (CH/Sac), 130.6 (CH/Sac), 131.3 (CH/Sac), 135.4 (C/Sac), 145.3 (C–S/Sac), 163.9 (CN_3^+), 170.0 (C=O/Sac). – Anal. for $C_{34}H_{62}N_4O_3S$ (606.9) × H_2O: calcd. C 65.34, H 10.32, N 8.96; found C 65.17, H 10.07, N 9.28.

Acknowledgements

The present work was funded by the Bundesministerium für Bildung und Forschung (Programm: Innovationen als Schlüssel für Nachhaltigkeit in der Wirtschaft. Verbundprojekt: Neuartige ionische Flüssigkeiten als innovative Reaktionsmedien für die Technische Organische Chemie. Förderkennzeichen 01RI05176). We are indebted to BASF SE, Ludwigshafen, for the gift of chemicals.

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