

---

Review

# Ionic Liquids based on the Concept of Melting Point Lowering due to Ethoxylation

Manuel Rothe<sup>1</sup>, Eva Müller<sup>1</sup>, Patrick Denk<sup>1</sup> and Werner Kunz<sup>1,\*</sup>

<sup>1</sup> Institute of Physical and Theoretical Chemistry, Faculty of Chemistry and Pharmacy, University of Regensburg, D-93040 Regensburg, Germany; Manuel.Rothe@ur.de (M. R.); Eva.Mueller@ur.de (E. M.); Patrick.Denk@ur.de (P. D.)

\* Correspondence: Werner.Kunz@ur.de (W. Kunz)

**Abstract:** Most of the commonly used Ionic Liquids (ILs) contain bulky organic cations with suitable anions. With our COMPLET (Concept of Melting Point Lowering due to Ethoxylation), we follow a different approach. We use simple, low-toxic, cheap and commercially available anions of the type  $C_x(EO)_yCH_2COO^-$  to liquefy presumably any simple metal ion, independently of its charge. In the simplest case, the cation can be sodium or lithium, but synthesis of Ionic Liquids is also possible with cations of higher valences such as transition or rare earth metals. Anions with longer alkyl chains are surface active and form surface active ionic liquids (SAILs), which combine properties of ionic and nonionic surfactants at room temperature. They show significant structuring even in their pure state, i.e. in the absence of water or any other added solvent.

This approach offers new application domains that go far beyond the common real or hypothetical use of classical Ionic Liquids. Possible applications include the separation of rare earth metals, the use as interesting media for metal catalysis, or the synthesis of completely new materials (for example in analogy to metal organic frameworks).

**Keywords:** ionic liquids; surface active ionic liquids (SAILs); room temperature ionic liquids (RTILs); alkyl ethylene glycol ether carboxylates; rare earth metals, transition metals, colloids, green chemistry

---

## 1. Introduction

Some years ago, one of the authors of the present paper co-authored a publication entitled *The hype with Ionic Liquids as solvents* [1]. Indeed, sometimes it seems that this topic is (ab-)used as a machinery to increase the number of publications and the researchers' impact factors rather than providing useful information about basic concepts or potential applications.

Today, the majority of colleagues agree that Ionic Liquids are not necessarily "green". Their synthesis usually is "red" and involves many steps and their lacking vapour pressure is not always a favourable property, because they cannot be separated by distillation. Further, they are often quite toxic, badly biodegradable etc.

However, they also undoubtedly have advantages. They enormously widen the spectrum of available liquids at room temperature. Although there is a general tendency to limit more and more the number of industrially used solvents and liquids, ILs may provide alternatives to currently applied and well-known ones. In this sense, their role as "designer solvents" may be justified, provided that it is rigorously checked that existing – usually cheaper – classical solvents cannot fulfil equally well the intended purpose.

So why do we need ILs?

First of all, and almost trivial: they provide the opportunity to dissolve certain solutes better than conventional solvents, often by means of special solute-solvent interactions. So, a) the liquid state matters and b) the solubility performance. Compared to these

features, the fact that the liquid consists of ions and therefore that electrostatic interactions may play a prominent role, is (often) of minor importance, except e.g., in electrochemistry. Second, and sometimes important and useful: the liquid may be structured in a way that goes beyond structuring in conventional low-molecular weight liquids. For example, there are surface-active, amphiphilic ILs (SAILs), where the imidazolium ring is connected to one or two long alkyl-chains thus creating cationic surfactants with convenient, usually small negatively charged counterions, mostly halides. Whereas these molecules may have some relevance when diluted in water (where they have some interesting properties, because of the smearing of the positive charges throughout the imidazolium ring), see [2] and references there, the current application in its pure IL state is rather limited.

In light of the demands and the quest for new room-temperature liquids and solvents, it seems evident to look for alternative approaches to ILs that avoid the inherent shortcomings, such as laborious synthesis and purification and the limitation that always more or less complex organic cations are required. These facts motivated us to follow a different strategy: instead of lowering the melting points of salts via the bulkiness of the *cations* with, as a consequence, an increase of the solid-state Gibbs energy due to hindered packing, we lower the Gibbs energy of the liquid state by increasing the entropy of the *anions* [3]. It is, in fact, an already established concept and partly explains the relative success of the so-called Akypo™ surfactants, commercialised by the Japanese company Kao Chemicals. Note that the concept can also be applied to cations, but this is not part of the present paper [4].

The general chemical structure of the molecules is the following:  $M^+ C_xEO_yCH_2COO^-$ , which we will call alkyl ethylene glycol ether carboxylates in the following. Usually, these substances are commercialised as neutral acids, i.e.  $M^+ = H^+$ . Most interestingly,  $M^+$  can be any type of cation, even as simple as  $Na^+$ ,  $Li^+$ ,  $K^+$ ,  $NH_4^+$  etc., but it can be also a complex cation and even a cationic surfactant. In the latter case, one can generate “true” cat-anionics, i.e. a mixture of cationic and anionic surfactants without any further counterions and this combination being even liquid at room temperature.

Let's have a closer look at the anion. Evidently, if  $x \geq 8$ , the anion is a surfactant, independently of  $y$ . But there are also very short anions available with  $x = 1-6$  only. Then, the resulting ILs behave as hydrotropes or as “simple” more or less unstructured solvents (at least one would not expect any mesoscopic structuring). To have them be liquid at room temperature, a sufficient number of ethylene glycol groups (EO) is mandatory. These groups are not only significantly hydrated in water thus ensuring a high water solubility, they exhibit a *high conformational entropy even in the pure state*. This is the secret behind their low melting points: they lose this entropy upon freezing, which is (Gibbs) energetically unfavourable. We called this approach to ILs *Concept of Melting Point Lowering due to Ethoxylation* (COMPLET) [3,5].

Compared to the “classical” concept to conceive ILs, several advantages are evident:

- (i) The ingredients are readily available. Akypos are quite cheap and sold in tons. A simple mixing with alkali hydroxides and subsequent (freeze) drying is sufficient. No laborious synthesis and purification are necessary.
- (ii) ILs can be made with simple cations and, as we will demonstrate in the following, even with di- and trivalent cations.
- (iii) The ILs are of low toxicity and readily biodegradable so that they can be even used in cosmetics, of course, only with a convenient cation.
- (iv) The anion in the IL can be surface active (and thus structuring) and can be liquid even with a surface-active cation forming “true cat-anionics” without further counter-ions.
- (v) Some of them are even of very low viscosity at room temperature.

In the following, we discuss three different cases. In the first case, we consider ILs with metal cations of different valency, in the second case, surface active ILs based on the

COMPLET concept, and finally, a particular case, where a partly protonated IL consists of direct micelles even in its pure state.

## 2. Ionic liquids with metal ions of different valency

Ionic Liquids are often praised for their flexibility and customisability, to the point of being called 'designer solvents'. In reality however, this is only true to a degree. While a variety of properties can be achieved with conventional ILs, their makeup, and especially the strategy behind them, is often quite limited. Only a few choice cations act as the 'heart' of nearly every 'modern' Ionic Liquid, modified to suit the desired application. Besides some phosphonium- and ammonium-based ILs, the lion's share possesses an imidazolium cation as their 'builder ion'. These ions can be modified and customised to a high degree and reliably lead to compounds with sufficiently low melting points to be classified as ionic liquids.

If one desires to incorporate metal ions as part of their ionic liquids, however, a problem arises: metal ions also carry positive charges and are thus inherently incompatible with all conventional 'builder ions'. Naturally, there are established ways to circumvent this issue. The metal cations can be incorporated into larger complexes with a single negative excess charge, which is then compensated by one of the conventional 'builder ions'. This strategy is often employed in the context of transition metals, which usually prefer higher oxidation states. A second common solution to the incompatibility issue is to skip the additional complexation compounds, and instead to attach residues to the 'builder ion' which can bind to the metal ions [6-8].

Some arguments can be made against these two strategies. The transformation into a negatively charged complex adds additional compounds into the mix. They can alter the properties of the metal, for example in catalytic applications, or introduce unwanted ions into the IL. Complexation by a sidechain of the main 'builder ion' may allow the direct incorporation of bare metal ions, avoiding this issue. But as the IL exists independently of the metal ion, one can also argue that instead of forming an ionic liquid *with* that metal ion, an IL is made that can only *solubilise* it instead.

Ideally, one would combine an anionic builder ion *directly* with the bare metal cation. Although avoiding the aforementioned issues, another one is introduced: many metal ions carry more than a single charge. The reason why this is an issue lies once again in the conventional concept for ionic liquids: they usually share a 1:1 stoichiometry. While ionic liquids with higher charges do exist, they are usually achieved by the simple linkage of several 'builder ions' [7,8].

With our alkyl ethylene glycol ether carboxylate salts, all these issues can be avoided. As they are built on a different concept, relying on *entropy* differences of the liquid and solid phases instead of *enthalpy* differences, they are much more flexible, especially when it comes to the combination with different cations. With  $C_8EO_5CH_2COO^-$  ([C8E5c]), we put an anion at the centre of the ionic liquid, and can easily combine it with a variety of metal ions. The COMPLET also allows for a deviation of the classical 1:1 stoichiometry, and di- and trivalent transition and rare earth metals ([REM]) can be easily incorporated ( $M = Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Y^{3+}, La^{3+}, Dy^{3+}, Eu^{3+}, Gd^{3+}$ ). The synthesis of these ionic liquids is as simple as it can be: the free acid [H][C8E5c] is mixed with a basic metal salt, usually a hydroxide or carbonate, and stirred for several hours under gentle heating. Figure 1 shows a selection of typical divalent Ionic Liquids based on the COMPLET ( $M^{2+} = Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}$ ).



**Figure 1.** Typical COMPLET-based ionic liquids containing divalent transition metal ions.

The resulting ILs show very diverse properties and ion-specific effects. As an example, the dynamic viscosities at 15 °C range from low, in the cases of [Dy][C8E5c]<sub>3</sub> (181 mPa s) or [Cu][C8E5c]<sub>2</sub> (849 mPa s), to high, in the cases of [Eu][C8E5c]<sub>3</sub> (126.6 Pa s) or [La][C8E5c]<sub>3</sub> (152.2 Pa s), and very high, in the case of [Mn][C8E5c]<sub>2</sub> (429.3 Pa s) [9]. The viscosity of a liquid is a measure of the mobility of its molecules, and as such it can provide some basic information about how the ILs may be structured. If the viscosity is high, the molecules within the liquid cannot freely flow past one another, and it is reasonable to assume that multiple metal centres are crosslinked via the alkyl ethylene glycol ether carboxylates.

To better understand the mobility within the liquid, specifically the ion mobility, the viscosity measurements can be supplemented with the measurement of electrical conductivities. The combination of these two mobilities, so the general molecular mobility given by the viscosity and the ion mobility given by the electrical conductivity, provides information about the association of the ions in the IL. In an ideal case with full disassociation of the anion(s) and the cation, the system behaves like a strong electrolyte. In a double logarithmic plot of the molar conductivity  $\Lambda$  against the fluidity  $\eta^{-1}$ , also called a *Walden Plot*, this behaviour is represented by a line of unit slope. Such ILs are also often termed 'good' ionic liquids. In contrast, 'poor' ionic liquids show large negative deviations from this ideal line (often also 'KCl line') as a result of ion pairing [10,11]. It is important to keep in mind that this classification into 'good' or 'poor' does not imply the quality of the substance, but rather is a measure of its ionicity—a spectrum from fully ionic to molecular liquids.

For three of the above ionic liquids, such a Walden Plot has been previously created and can be seen in Figure 2 [9]. The chosen ILs are all based on rare earth metals, which are generally known to have quite similar properties. These similarities do not hold true in the case of our ILs. Not only do they possess vastly different fluidities, but also vary quite strongly in their measures of ion association. Both [Eu][C8E5c]<sub>3</sub> and [Y][C8E5c]<sub>3</sub> show significant negative deviations from the ideal line, indicating quite strong association of the ions. [La][C8E5c]<sub>3</sub> however, remarkably displays only small deviations, and consequently, strong dissociation of the ions. This difference in ion mobilities and association presumptively is rooted in structural differences within the IL. It is known that related ionic liquids with alkali metals form both interconnected networks and globular complexes for sodium and potassium, respectively [12]. This difference in structure is also reflected in the difference in melting points – the sodium salt melts at -57 °C, and the potassium salt at +60 °C [13]. Transition metals, and especially rare earth metals have quite versatile complexation behaviour and allow for much more diverse structures.

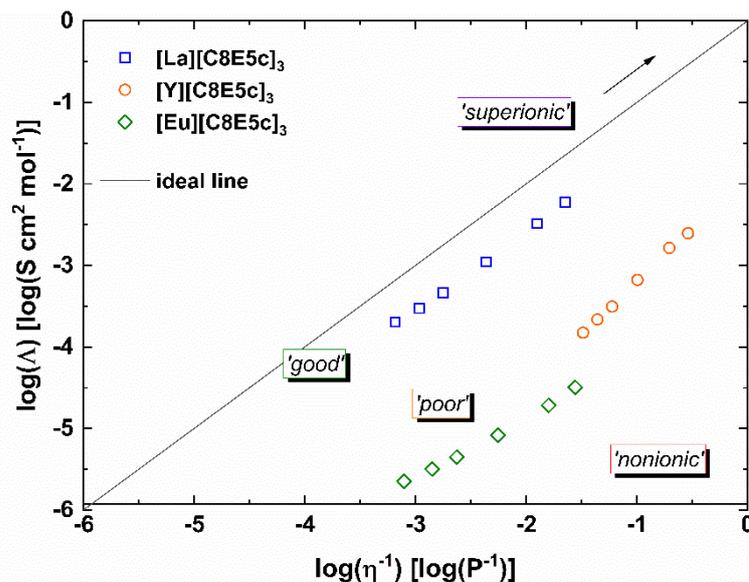


Figure 2. Walden Plot of selected rare earth metal ionic liquids in a range of 15-60 °C in comparison to the ideal KCl line.

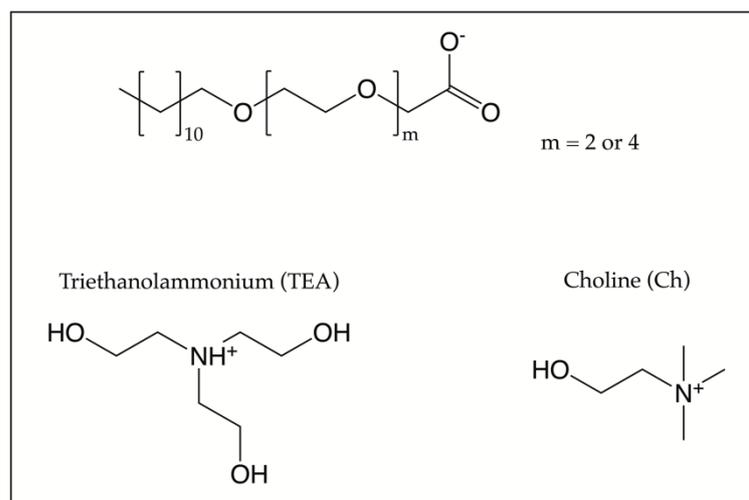
The diversity in properties does not end in these transport properties, but extends into other attributes with more direct application as well. We have previously shown that the solubilities of [REM][C8E5c]<sub>3</sub> ILs in different solvents, or rather the resulting octanol/water partition coefficients  $P$ , are highly dependent on the associated cation, see Figure 2 [9]. These proof-of concept separation experiments have already shown that the otherwise resource- and labour-intensive separation of rare earth metals is accessible with the use of alkyl ethylene glycol ether carboxylates. The partition coefficients are greatly impacted by the presence of other ions, providing a highly sensitive and tunable system. The unique structure of the [C8E5c] anion also makes it responsive to changes in pH, due to its carboxylic acid, and changes in temperature, due to its ethylene glycol chain.

This novel class of ionic liquids shows great promise in a multitude of applications due to their unique approach to liquefying metal ions. In combination with suitable metals, alkyl ethylene glycol ether carboxylate ionic liquids could be used as fluorescent dyes, in synthesis and catalysis, or as precursors for structured ceramics or nanoparticles. It is clear that the properties of the ionic liquids strongly depend on the choice of cation, and consequently, their application. However, the influence of the anion should not be forgotten: it is indubitably responsible for much of the solution and structuring behaviour, and has also shown to greatly impact fluorescence, enabling fluorescence in the visible spectrum for otherwise non-luminescent metal ions [9]. Variation and modification of the anion will surely enable the production of tailor-made, metal-based ionic liquids.

### 3. Surface active alkyl ethylene glycol ether carboxylates

In Reference [3], we have shown that the COMPLET concept can be used to liquefy cationic surfactants such as long-chain alkylammonium ones by combining them with short-chain methyl tetra ethylene glycol ether carboxylates. How to incorporate directly ethylene glycol groups into *cationic* surfactants to liquefy them with any type of anion, will be subject of several forthcoming papers, e.g. [4].

By contrast, in the present section, we focus on surfactants of the type dodecyl ethylene glycol ether carboxylate with 2 or 4 ethylene glycol groups ([C12E2c] or [C12E4c]) and either choline (Ch) or triethanolammonium (TEA) as counterions, see Figure 3.

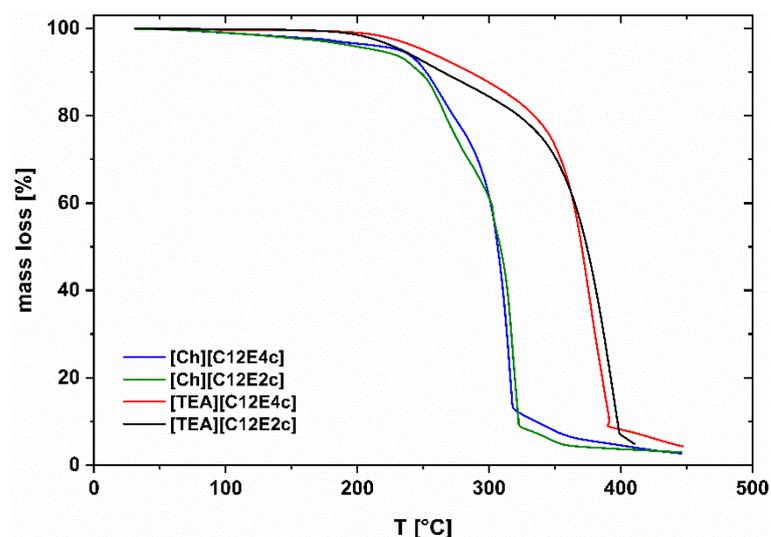


**Figure 3.** The anions and cations giving SAILs, as discussed in this section.

The **thermal stability** is an important feature of Ionic Liquids. Commonly used organic solvents are characterized by either a high vapour pressure or a low boiling point or both. Since Ionic Liquids do not have an appreciable vapour pressure, they can be applied in liquid state up to the temperature of thermal decomposition [8].

Therefore, thermal stability of the here discussed SAILs was studied using a thermogravimetric analyser TGA 7 from Perkin-Elmer (Waltham, Massachusetts, USA). Samples were measured at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ , applying a continuous nitrogen flow. Decomposition temperatures were determined using onset points of mass loss, being defined as the intersection of the baseline before decomposition and the tangent to the mass loss versus temperature.

All of the tested compounds showed decomposition only above or at least close to  $200 \text{ }^\circ\text{C}$ . Decomposition temperatures of common Ionic Liquids can be found in the same range [14]. In case of the pure substances the highest stability was found for the TEA ILs followed by Ch. No significant difference in thermal destruction occurred for Ch or TEA species with either two or four ethoxy units in the anionic part, see Figure 4.



**Figure 4.** Temperature-dependent mass loss curves. Comparison of different counterions and degree of ethoxylation.

As can be seen in Figure 4, TEA leads to more resistant derivatives, while the point of decomposition decreases by  $40 \text{ }^\circ\text{C}$  for choline species. Table 1 contains additional data for the four SAILs presented here. Further details about the experimental methods and

the characterisation of more SAILs can be found in [15]. Note that all of the SAILs have **glass transition temperatures** far below 0 °C, exhibit high **viscosities** at room temperature and, for anionic surfactants, relatively low **critical micelle concentrations** (cmc), when dissolved in water. They all exhibit a **pseudoplastic behaviour** at room temperature.

**Table 1.** Decomposition and glass transition temperatures as well as viscosities at two different temperatures of the four considered salts (SAILs) and finally their rheological behaviour. For aqueous solutions, also their critical micelle concentrations are given at room temperature.

Composition	T decomp. [°C]	T glass trans. [°C]	cmc [mol/L]	Viscosity 20 °C [Pa s]	Viscosity 80 °C [Pa s]	Rheology
[TEA][C12E2c]	345	-39.0	$2 \cdot 10^{-4}$	~ 100	~ 4	pseudoplastic
[Ch][C12E2c]	307	-44.0	$2 \cdot 10^{-4}$	~ 30	~ 5	pseudoplastic
[TEA][C12E4c]	345	-42.0	$2 \cdot 10^{-4}$	~ 60	$30 \cdot 10^{-3}$	pseudoplastic $\leq 70$ °C newtonian $> 70$ °C
[Ch][C12E4c]	309	-49.5	$2 \cdot 10^{-4}$	~ 80	$10 \cdot 10^{-3}$	pseudoplastic $\leq 60$ °C newtonian $> 60$ °C

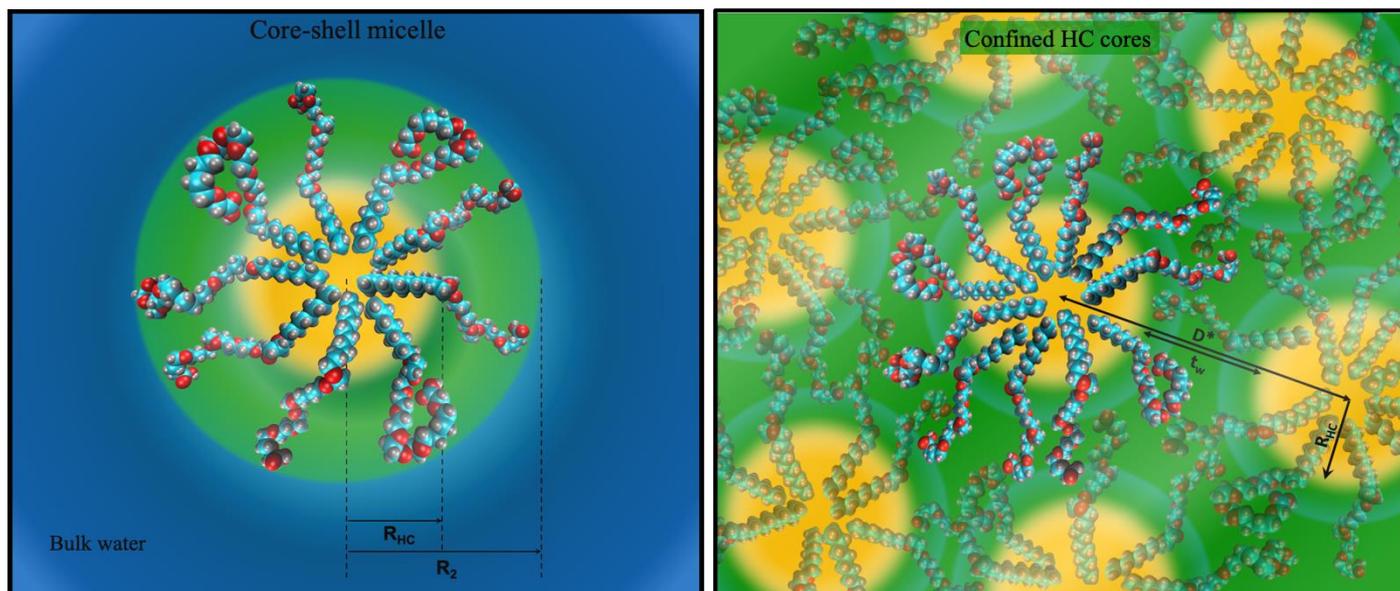
#### 4. The special case of $M^+ C_8EO_8CH_2COO^-$

With  $x = 8$  and  $y = 8$ , octyl octaethylene glycol ether carboxylic acid ( $C_8EO_8CH_2COOH$ ) with its commercial name Akypo LF2, is a surfactant comprised of a rather small hydrophobic and a much larger hydrophilic moiety. The comparatively long ethylene glycol chain ensures a sufficiently low melting point to keep the surfactant in its liquid state at room temperature, even in absence of water. As demonstrated above,  $C_8EO_8CH_2COOH$  ([H][C8E5c]) (section 2) and similar molecules (section 3) can be deprotonated and combined with any metal cation, while retaining their liquid state, rendering them room temperature ionic liquids. Unsurprisingly, Akypo LF2 ([H][C8E8c]) can be treated similarly to obtain ionic liquids.

In a recent paper [16], we reported on the **aqueous phase behaviour** of [H][C8E8c] and elucidated its micro-structuring over a wide range of concentrations by small-angle x-ray scattering (SAXS). Within the scope of that work, we also analysed the effect of  $CaCl_2$  and NaOH on the phase behaviour. Apart from a small coacervation regime at very low surfactant concentrations ( $< 1$  wt%), the acid form features a phase behaviour similar to that of the non-ionic surfactant  $C_8EO_8$  [17] with a typical clouding phenomenon. The lower critical solution temperature (LCST) of [H][C8E8c] was found to be 66 °C, thus being significantly lower than the LCST of 96 °C reported for  $C_8EO_8$ . This difference can be attributed to enhanced intermicellar interactions, enabled by the additional carboxylic acid moieties.  $Ca^{2+}$  ions can act as intermicellar bridging agents between two carboxylate functions, as such lowering the LCST to 49 °C. As opposed to that, deprotonation of [H][C8E8c] with NaOH enhances its ionic character, completely suppressing the clouding phenomenon for  $[Na]_{0.5}[H]_{0.5}[C8E8c]$ . Yet, the phase behaviour is remarkably simple in all cases. No liquid crystalline or reversed phases are observed, and the systems are isotropic, micellar liquids of relatively low viscosity at all ratios with water and all temperatures (above the critical micelle concentration and below the cloud point).

A careful SAXS study revealed that [H][C8E8c] forms **direct spherical micelles** of constant size (hydrocarbon core radius  $R_{HC} \approx 1.2$  nm, aggregation number  $N_{agg} \approx 30$ ) and shape **over the whole concentration range**. Only at concentrations above 70 wt%, when there is no longer any bulk water due to hydration of EO-groups, the size starts to decrease gradually. In the almost water-free state,  $N_{agg}$  is reduced to 8 and  $R_{HC}$  is reduced to approximately 0.8 nm. Obviously, the normal core-shell micelles cannot persist without any bulk water. Spherical micelles are then only possible, if the hydrophilic headgroups interdigitate and form a hydrophilic medium of more or less hydrated headgroups, in which the hydrophobic cores, consisting of hydrocarbon chains, are dispersed. Indeed, we could substantiate this idea through a combination of SAXS and vapor pressure

osmometry measurements. Figure 5 is a sketch of the observed structures at high and low water concentrations.



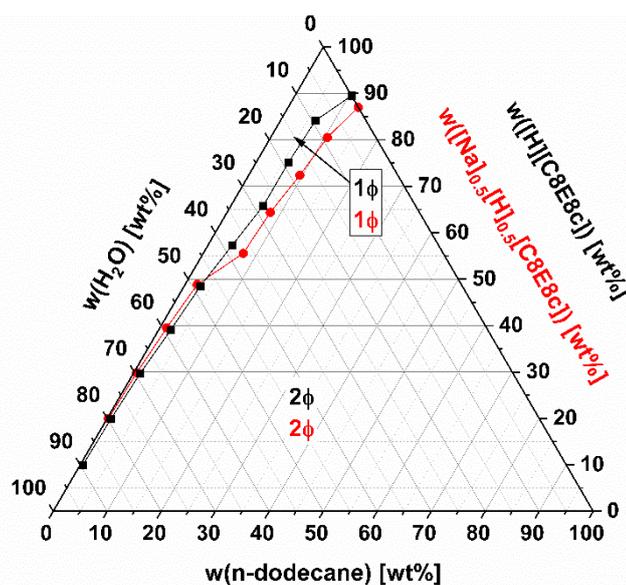
**Figure 5.** Scaled sketch of the two regimes observed in binary [H][C8E8c] water solutions. Left: the common core-shell structuring of direct micelles: a hydrocarbon core ( $R_{HC} = 1.2$  nm, shown in yellow) is surrounded by a hydrated ethylene glycol shell (shown in green); the bulk represented in blue contains monomers at cmc. Right: the confined hydrocarbon core (HC) regime observed in water-poor solution with interdigitated headgroups and the absence of bulk water; in this regime, the inter-particle distance gives a scattering peak at  $D^* = 2\pi/q_{max}$ . As could be inferred from osmotic pressure measurements, the compression of the water-poor ethylene glycol layer ( $t_w$ ) is responsible of the stability of the structure. The Figure was taken from [16].

The effects of  $CaCl_2$  addition and transformation of [H][C8E8c] to  $[Na]_{0.5}[H]_{0.5}[C8E8c]$  ( $pH = pK_a \approx 4$ ) can be summarised as follows. Neither the addition of  $CaCl_2$  nor the addition of NaOH changes the general structuring of the system. However, both partially suppress interdigitation and decrease the area per molecule  $a$ . In this case, a reduction of  $a$  corresponds to an increase of  $N_{agg}$ . Yet, the mechanism leading to the partial suppression of interdigitation is different in both cases.  $Ca^{2+}$  ions can bridge carboxylate functions between or within micelles, inhibiting interdigitation either way. Nevertheless,  $Ca^{2+}$  enhances micellar attraction. Deprotonation of [H][C8E8c] with NaOH, on the other hand, enhances micellar repulsion by increasing the charge, consequently impeding headgroup interdigitation at the same time.

Since the publication of our referenced work [16],  $[Na][C8E8c]$  and  $[Ca][C8E8c]_2$  were prepared with less than 0.5 wt% residual water. Both of them are isotropic ILs above their glass transition point.  $[Na][C8E8c]$  is liquid above 27.5 °C, whereas  $[Ca][C8E8c]_2$  is already liquid above 19.5 °C. These ionic liquids will be investigated by SAXS in the future, but extrapolation of our published data suggests that they also consist of spherical hydrocarbon cores, dispersed in a hydrophilic medium of interdigitated headgroups. If this is the case, these ionic liquids are highly interesting, because they possess (a) hydrophobic nanodroplets dispersed in a hydrophilic medium with a large interface and (b) the carboxylate functions enable charge-transfer between both domains, since the EO-chains are highly flexible. Owing to those features, the [C8E8c] SAILs seem to be very promising solvents for catalytic purposes. Nanoparticle synthesis in such a confined environment may also be conceivable.

In regard to catalysis of organic reactions, it is also worth considering the phase behaviour of the SAILs on the addition of hydrophobic solvents and water. Ternary phase diagrams of the systems [H][C8E8c] /  $H_2O$  / n-dodecane and  $[Na]_{0.5}[H]_{0.5}[C8E8c]$  /  $H_2O$  / n-dodecane at  $T \approx 23^\circ C$  are given and compared in Figure 6. Note that the glass transition of dry  $[Na]_{0.5}[H]_{0.5}[C8E8c]$  (< 0.5 wt%  $H_2O$ ) is shifted to lower temperatures compared to

that of neat  $[\text{Na}][\text{C8E8c}]$ . It is liquid at temperatures above approximately 22–23 °C. In both cases, at any surfactant concentration, only a certain amount of n-dodecane can be solubilized. Any excess n-dodecane phase separates. This can be explained by the incorporation of n-dodecane into the hydrophobic cores of the (interdigitated) micelles, which is only possible to a certain extent, as the packing of the surfactant molecules is constrained and most likely only allows spherical structures. Further, it is likely that the separating n-dodecane phase contains almost no surfactant, due to its inability to form reversed structures. Since there is also a phase separation in the case of the water-free SAIL, unlike for example the case of the non-ionic surfactant  $\text{C}_8\text{EO}_6$ , which is completely miscible with n-dodecane [18], a simple extraction of possible reaction products might be feasible.  $[\text{H}][\text{C8E8c}]$  can uptake about 10 wt% n-dodecane, and  $[\text{Na}]_{0.5}[\text{H}]_{0.5}[\text{C8E8c}]$  up to 13 wt%.



**Figure 6:** Ternary phase diagrams of  $[\text{H}][\text{C8E8c}]/\text{H}_2\text{O}/\text{n-dodecane}$  (■) and  $[\text{Na}]_{0.5}[\text{H}]_{0.5}[\text{C8E8c}]/\text{H}_2\text{O}/\text{n-dodecane}$  (●) at a temperature of 23 °C ( $\pm 1$  °C). Concentrations are given in wt%. The precision in  $w(\text{n-dodecane})$  is usually  $\pm 0.5$  wt%, whereas the deviation of the other weights is negligible.  $1\phi$  denotes a monophasic system, and  $2\phi$ , realms of existence of two liquids in equilibrium.

## 5. Conclusion and outlook

Compared to classical ionic liquids (ILs), the ILs based on COMPLET (Concept of Melting Point Lowering due to Ethoxylation) offer numerous advantages. They are very easy to prepare, they are cheap, of low toxicity, and the organic part is readily biodegradable. Further, they can be used to liquefy virtually any cation, be it mono-, di- or triple charged, at room temperature. Since the ILs presented here are liquified via the high flexibility of the organic anions, simple cations such as  $\text{Na}^+$  and  $\text{Li}^+$  can be used as well as  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  or  $\text{Eu}^{3+}$  or, probably, any other cation that is interesting for catalysis or that must be extracted and recovered. The anions can also be surface-active. Although surface-active ILs (SAILs) are already known, the COMPLET-based SAILs offer anionic surfactants, which are much more relevant for large applications than cationic ones.

On the other hand, COMPLET-based ILs offer several advantages just as other ILs: they are of low volatility and liquid and stable over a wide temperature range.

Given all these advantages, we believe that this type of ILs will have a significant future and impact on improved industrial processes and products.

**Funding:** This research received no external funding.

**Data Availability Statement:** Additional data are available on request to the authors.

**Acknowledgments:** The authors would like to thank Kao Chemicals, particularly Thomas Myrdek, for generously providing the alkyl ethylene glycol ether carboxylates free of charge.

**Conflicts of Interest:** The authors declare no conflict of interest.

**Sample Availability:** Samples of the compounds are not available from the authors.

## References

1. Häckl, K.; Kunz, W. Some aspects of green solvents. *Comptes Rendus de l'Académie des Sciences (France) Chimie* **2018**, *21*, 572-580. <https://doi.org/10.1016/j.crci.2018.03.010>
2. Kunz, W.; Zemb, T.; Harrar, A. Using ionic liquids to formulate microemulsions: Current state of affairs. *Current Op. Coll. Interf. Sci.* **2012**, *17*, 205-211. <https://doi.org/10.1016/j.cocis.2012.03.002>
3. Müller, E.; Zahnweh, L.; Estrine, B.; Zech, O.; Allolio, C.; Heilmann, J.; Kunz, W. Oligoether Carboxylate Counterions: An Innovative Way Towards Surfactant Ionic Liquids. *J. Molec. Liq.* **2018**, *251*, 61-69. <https://doi.org/10.1016/j.molliq.2017.12.037>
4. Braun, L.; Kellermeier, M.; Engelhardt, N.; Oetter, G.; Engert, S.; Kunz, W. A new type of cationic surfactant: the insertion of ethoxy groups as a way towards soluble catanionic mixtures at equimolar ratio. (*in preparation*)
5. Klein, R.; Zech, O.; Maurer, E.; Kellermeier, M.; Kunz, W. Oligoether Carboxylates – Task Specific Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2011**, *115*, 8961-8969. <https://doi.org/10.1021/jp200624g>
6. Binnemans, K. Lanthanides and Actinides in Ionic Liquids. *Chem. Rev.* **2007**, *107*, 2592-2614. <https://doi.org/10.1021/cr050979c>
7. Prodius, D.; Mudring, A.V. Rare earth metal-containing ionic liquids. *Coord. Chem. Rev.* **2018**, *363*, 1-16. <https://doi.org/10.1016/j.ccr.2018.02.004>
8. *Ionic Liquids in Synthesis*, 1st ed.; Wasserscheid, P.; Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2002.
9. Rothe, M.; Tress, M.; Allacher, C.; Nürnberger, P.; Kunz, W. Ionic Liquids [M<sup>3+</sup>][A<sup>-</sup>]<sub>3</sub> with three-valent cations and their possible use to easily separate rare earth metals. *Chem. – A Eur. J.* (submitted in May 2021)
10. Austen Angell, C.; Ansari, Y.; Zhao, Z. Ionic Liquids: Past, present and future. *Faraday. Discuss.* **2012**, *154*, 9-27. <https://doi.org/10.1039/C1FD00112D>
11. Xu, W.; Cooper, E.I.; Austen Angell, C. Ionic Liquids: Ion Mobilities, Glass Temperatures, and Fragilities. *J. Phys. Chem. B* **2003**, *107*, 6170-6178. <https://doi.org/10.1021/jp0275894>
12. Zech, O.; Hunger, J.; Sangoro, J.R.; Iacob, C.; Kremer, F.; Kunz, W.; Buchner, R. Correlation between polarity parameters and dielectric properties of [Na][TOTO] – a sodium ionic liquid. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14341-14350. <https://doi.org/10.1039/C0CP00840K>
13. Zech, O.; Kellermeier, M.; Thomaier, S.; Maurer, E.; Klein, R.; Schreiner, C.; Kunz, W. Alkali Metal Oligoether Carboxylates – A New Class of Ionic Liquids. *Chem. – A Eur. J.* **2009**, *15*, 1341-1345. <https://doi.org/10.1002/chem.200801806>
14. Zhou, Z.; Matsumoto, H.; Tatsumi, K. Low-Melting, Low-Viscous, Hydrophobic Ionic Liquids: Aliphatic Quaternary Ammonium Salts with Perfluoroalkyltrifluoroborates. *Chem. – A Eur. J.* **2005**, *11*, 752-766. <https://doi.org/10.1002/chem.200400817>
15. Maurer, E. Melting and Aggregation Behaviour of Novel Bio-Compatible Anionic, Cationic and Catanionic Surfactant Systems. PhD Thesis, University of Regensburg, Germany, 2011.
16. Denk, P.; El Maangar, A.; Lal, J.; Kleber, D.; Zemb, T.; Kunz, W. Phase diagrams and microstructures of aqueous short alkyl chain polyethylene glycol ether carboxylate and carboxylic acid triblock surfactant solutions. *J. Colloid Interface Sci.* **2021**, *590*, 375-386. <https://doi.org/10.1016/j.jcis.2021.01.061>
17. Mitchell, D.J.; Tiddy, G.J.T.; Waring, L.; Bostock, T.; McDonald, M.P. Phase behaviour of polyoxyethylene surfactants with water. Mesophase structures and partial miscibility (cloud points). *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 975-1000. <https://doi.org/10.1039/F19837900975>
18. Marland, J.S.; Mulley, B.A. A phase-rule study of multiple-phase formation in a model emulsion system containing water, n-octanol, n-dodecane and/a non-ionic surface-active agent at 10 and 25°. *J. Pharm. Pharmacol.* **1971**, *23*, 561-572. <https://doi.org/10.1111/j.2042-7158.1971.tb08718.x>