

Low Impact and highly recyclable Surfactant-based supramolecular eutectogels for Iodine removal

*Salvatore Marullo,^a Matteo Tiecco,^{*b} Raimondo Germani^b and Francesca D'Anna^{*a}*

[a] Università degli Studi di Palermo, Dipartimento di Scienze Biologiche, Chimiche e Farmaceutiche, Sezione di Chimica, Viale delle Scienze Ed. 17, 90128 Palermo (Italy)

[b] Department of Chemistry, Biology and Biotechnology, Università degli Studi di Perugia, via Elce di Sotto 8, 06124 Perugia (Italy)

Corresponding authors

Prof. Francesca D'Anna, e-mail francesca.danna@unipa.it

Dr. Matteo Tiecco, e-mail matteotiecco@gmail.com

Abstract

In this work we screened several surfactants for their ability to harden Deep Eutectic Solvents (DESs). We found cetyldiethanolamine-N-oxide as the best candidate, a compound with known anti-microbial activity and low toxicity, which was able to form eutectogel in four DESs. Characterization of the gels obtained in terms of thermal stability, rheology and gelation kinetics and showed a prominent influence of the nature of the hydrogen bonding accepting and donating components for the first two parameter and the other one, respectively. Then, we assessed the eutectogels for their ability to adsorb I₂, as a model for its radioactive nuclides, from apolar solvent solutions. The best performing gel

allowed fast and thorough removal of I₂, over a broad range of initial concentrations. This gel displayed a maximum adsorption capacity of 280 mg/g, competitive with most gel-based sorbent reported in the literature for the adsorption of iodine. Interestingly, the eutectogel proved to be highly recyclable, it could be regenerated and reused without loss in performance.

Keywords: Deep Eutectic Solvents • Supramolecular Gels • Surfactants • Adsorption • Iodine removal.

1. Introduction

The presence of radioactive isotopes in the environment is a very important problem, due to the grave threat they pose on human health, and to the environment in general. In this context, a great interest of researchers is focused in the removal of radioisotopes of iodine like ¹³¹I and ¹²⁹I, deriving from nuclear fission processes in nuclear power plants,¹ and from medical diagnostics and therapy contexts.² In particular, ¹²⁹I raises concerns for its high persistence and half-life (1.57·10⁷ years), whereas ¹³¹I interferes with many metabolic pathways in humans.³ Based on these considerations, a considerable interest is currently devoted to find effective methods for the capture and removal of ¹³¹I and ¹²⁹I, from both gas-phase⁴ and solutions.⁵ To date, most of the works available in literature, rely on the use of suitable sorbents, i.e. solid materials onto which the harmful nuclides are transferred from gas streams or liquid waste. Adsorption methods for the removal of contaminants have the general advantages of low cost and energy demand, conjugated with simplicity of operation and, in many cases, high removal efficiency.^{5,6} The sorbent materials used for capture, removal and storage of radionuclides include bulk nanoporous materials like zeolites,⁷ aerogels^{8,9} and activated carbon,¹⁰ microporous materials such as carbon nanotube¹¹ or graphene oxide-composites,¹² as well as structurally flexible, sub-micro/microporous materials like metal-organic frameworks (MOFs)¹³⁻¹⁵ and porous coordination polymers (PCPs).¹⁶ Another emerging class of nanostructured sorbent materials is constituted by supramolecular gels.¹⁷⁻¹⁹ These materials, are originated by the self-

assembly of small molecules known as Low Molecular Weight Gelators (LMWGs) in diluted solutions, and are underpinned solely by non-covalent interactions. The self-assembly process features the aggregation of gelators to form a sample-spanning 3D-network able to trap high amounts of solvent molecules through capillary forces, so that solvent flow is arrested. Hence, although gels are prominently constituted by a liquid, their rheological behavior is closer to that of a solid. Gels find application in a vast array of fields, and due to their inherent nanostructure, they can also constitute excellent nanostructured sorbents and, in general, materials for environmental remediation.^{20,21} In this context, gels often possess convenient properties, such as high surface area, high removal capacity and possibility of being recycled.

Supramolecular gels are typically classified by the solvent in which they are prepared. According to this classification, gels can be named as hydrogels or organogels depending on whether they are prepared from solutions in water and organic solvents respectively. More recently, gels in non-conventional solvents have gained more interest, such as gels in ionic liquids, i.e. ionic liquid gels²² and in deep eutectic solvents (DESs),²³⁻²⁵ namely eutectogels.²⁶

DESs are mixtures of compounds melting at a definite temperature, lower than the ones of any individual components. They have aroused interest as sustainable, non-conventional solvents, because they are typically constituted by simple, cheap components, often derived from natural sources, with low or no toxicity. Moreover, their preparation only involves mixing of components, with no synthetic and purification steps. Formation of DESs involves the establishment of a hydrogen bond network between a hydrogen bond donor component (HBD), and a hydrogen bonding acceptor one (HBA), and share some convenient properties with ionic liquids, such as low volatility and flammability.

In the framework of our interest in gels in non-conventional solvents, we have shown that ionic liquid gels and eutectogels are efficient sorbents for a wide range of pollutants, such as dyes,^{27,28} pharmaceutically active compounds,^{29,30} Cr(VI)³¹ or sulfur compounds from fuels.³²

In this work, we describe the preparation and characterization of surfactant-based supramolecular eutectogels. Initially, we screened a wide range of surfactants as gelators for DES, to find the best candidate, i.e. cetyldiethanolamine N-oxide (Figure 1). The gelator-surfactant identified is well known for its low toxicity and antimicrobial activity, that has allowed its use in the formulation of topical germicides and inhibitors of body odor.^{33,34} We carried out gelation tests in a diverse range of DES and fully characterized the materials obtained in terms of gel-sol transition temperature, critical gelation concentrations, gelation kinetics, rheology and morphology. Then, we investigated their ability to adsorb molecular iodine from apolar solvent solution, using ¹²⁷I as model for the radioactive nuclides. We found that our eutectogels allow fast and thorough removal of iodine, and the best performing one was able to retain high removal efficiency over a broad range of initial I₂ concentrations, with a maximum adsorption capacity of 280 mg/g, competitive with most gel-based sorbent system for iodine reported in the literature, in terms of high efficiency and short time of contact. The best performing gel can be reused for at least 18 cycles, can be regenerated using a recommended solvent and then reused for further 20 cycles without significant loss in performance.

2. Materials and methods

Commercially available choline chloride, diethylene glycol, ethylene glycol, trimethylglycine, thymol, glycolic acid, tetrabutylammonium chloride, tetrabutylphosphonium chloride, (±) menthol, acetic acid, pyruvic acid, (±) lactic acid, dodecanoic acid and iodine were used without further purification. Commercially available solvents were used as received. Commercially available surfactants were purchased from Sigma-Aldrich and were recrystallised in acetone/methanol mixture prior use. The other non-commercial amphiphiles were synthesised following procedures reported elsewhere.³⁵⁻³⁸

2.1 Screening of Surfactants as gelators and tube inversion test

The solubilities of the surfactants were determined via subsequent additions of weighted amounts of solid amphiphiles to the DESs or to the HBD liquids. The solutions were then vigorously stirred at room temperature until homogeneous fluids were obtained. Whenever the solutions remained opaque or with precipitates, the liquids were heated and stirred at 50°C until they became homogeneous and remained in this status when they returned at 25°C. The maximum solubilities values were considered when the solutions remained opaque or showed precipitates even after heating.

The tube inversion test was performed via a qualitative determination of the fluidity of the samples after putting the containers upside down. The samples were put in same-sized vials at the same weight (approximately 3 grams in 7 mL vials of 1.2 cm diameter); whenever the fluids remained in the bottom of the vials for a time over 3 hours the systems were considered as plausible gels, while if the liquids flew down, they were considered as fluids at different apparent viscosity (see Table 1).^{39,40}

2.2 Gelation tests and T_{gel} determination

Gels were prepared by weighing into a screw-capped sample vial (diameter 0.5 cm) the suitable amount of surfactant and DES. The sample vial was heated in an oil bath, at a suitable temperature for 1h, until all the surfactant was dissolved. The vial was then kept at room temperature overnight. The tube inversion test method was used to assess gel formation.⁴¹ T_{gel} were determined by the falling drop method.⁴² A vial containing the preformed gel was placed upside-down in a water bath. The bath temperature was raised gradually (1 °C/ min) until the gel collapsed and flow was observed. T_{gel} values were reproducible within 1 °C.

2.3 Opacity Measurements

Opacity measurements were carried out with a spectrophotometer. The opacity of the gel phases was determined with UV-Vis measurements as a function of time, at a wavelength of 568 nm at a temperature of 25 °C. Samples for a typical measurement were prepared by injecting into a quartz

cuvette (light path 0.2 cm) the limpid hot solution of surfactant in DES. Spectra were recorded until gel formation. The gel phase obtained at the end of the measurement was stable after the tube inversion test.⁴¹

2.4 Rheology measurements

Rheological measurements were carried out on a strain-controlled rheometer using a Peltier temperature controller and a plate-plate tool. For a typical measurement, the gel was formed in a plastic blister pack, then the sample was transferred between the shearing plates of the rheometer. Rheological properties, such as strain and frequency sweep, were recorded at 25 °C. Rheological properties were recorded three times on three different aliquots of gels.

SEM images

SEM measurements were carried out on a PRO X PHENOM electronic scanning microscope, operating at 5 KV. Xerogels for each sample were obtained placing each gel on an aluminum stub, and then washing it with ethanol to remove the DES, following a previously reported procedure.^{27,43,44}

2.5 Iodine Adsorption tests

Iodine adsorption tests were carried out in vials by placing onto the 500 mg of preformed eutectogel (5 wt %), 1 mL of a 500 ppm iodine solution in hexane, at 25 °C. After a given time, an aliquot of solution was withdrawn, suitably diluted, then the relevant UV-vis spectrum was recorded. Concentrations were obtained based on a previously obtained calibration curve obtained by measuring the absorbance of hexane solutions of iodine at increasing concentrations. The same procedure was followed for the experiments at different initial concentration of iodine, and for the adsorption capacity determination.

To recycle the gel, after an adsorption run, the organic phase was removed and replaced with a fresh batch of iodine solution. Iodine-laden gels were regenerated by contact with portions of

2-methyltetrahydrofuran (3*0.5 mL). Each sample was then placed in an orbital shaker at 300 rpm for 5 minutes. Then, the organic phase was removed and the amount of iodine recovered was determined spectrophotometrically, based on a calibration curve previously obtained.

3. Results and discussion

The first step of this work was a screening of a set of amphiphilic molecules that might act as gelators of three DESs mixtures. The surfactants were chosen among a wide set of synthetic and commercially available amphiphiles for their capabilities to gel water, as reported in literature.^{37,45} The tested surfactants belong to different families of amphiphiles: *p*-alkyloxybenzyl- surfactants (*p*-dodecyloxybenzyltrimethylammonium bromide; *p*-octyloxybenzyltriethylammonium bromide); ethanol-headed surfactants (Hexadecyldimethylethanolammonium bromide; Hexadecylmethyldiethanolammonium methanesulfonate; Cetyltriethanolammonium bromide; Didodecylmethylethanolammonium bromide; Didodecylmethylethanolammonium chloride; N,N-dimethyl-N-hexadecyl-(D)-glucammonium methanesulfonate); *p*-dodecyloxybenzyl dimethylethanolammonium bromide that has both groups characteristics; and amphiphiles that can be considered also part of these groups but with N-oxide head (*p*-dodecyloxybenzyl dimethylamine N-oxide; Cetyldiethanolamine N-oxide). Cetyltrimethylammonium bromide was also tested as model cationic surfactant. The structures of these amphiphiles are reported in Table A.1.

The tested Deep Eutectic Solvents were: Choline Chloride/Diethylene Glycol (**ChCl/DEG**), 1/3 molar ratio); Choline Chloride/1,2-Propylene Glycol (**ChCl/PG**, 1/3 molar ratio); Choline Chloride/Glycerol (**ChCl/GLY**, 1/2 molar ratio).⁴⁶ In this preliminary screening these three choline chloride-based probe DESs were chosen for their low viscosity. This was because the possibility of forming gel phases was evaluated by the tube inversion test at the maximum solubility of the surfactant in the liquid; therefore, a high fluidity of the system facilitates the evaluation of the

increment of viscosity thanks to a possible self-assembly in DESs of these molecules. This qualitative approach was useful for its fastness and simplicity and represented a useful tool for a preliminary screening on a wide number of possible gelators.

In Table 1, the maximum solubility of the surfactants in the DESs mixtures and the apparent viscosity of the samples at these concentrations at 25°C are reported. The viscosity of the liquids without any added surfactant is also reported in the same table. The apparent viscosity was evaluated in a qualitative scale from one to five, considering as one those liquids that were really fluid and with five those mixtures that did not fall in the tube inversion test.⁴¹ In between these values, the mixtures that slowly or immediately fell down after the inversion of the samples are reported in scale. In the same Table the results of the dissolution of the surfactants in the liquid HBD components (Diethylene Glycol, 1,2-Propylene Glycol and Glycerol) of the DESs are reported in order to clarify the role of the HBA in the DESs' systems. In these manners it is possible to avoid any consideration that could be derived only from the HBD molecule of the DESs.

Table 1. Maximum solubility (M) and apparent viscosity of solutions of surfactants in DESs and in pure HBD liquids at 25°C; apparent viscosity qualitatively determined via tube inversion test: ● extremely fluid; ●● fluid; ●●● viscous; ●●●● extremely viscous; ●●●●● do not fall after tube inversion. ChCl/DEG = Choline Chloride / Diethylene Glycol (1/3 molar ratio); ChCl/PG = Choline Chloride/Propylene Glycol (1/3 molar ratio); ChCl/GLY = Choline Chloride/Glycerol (1/2 molar ratio); DEG = Diethylene Glycol; PG = Propylene Glycol; GLY = Glycerol.

Entry	SURFACTANT	ChCl/DEG		ChCl/PG		ChCl/GLY		DEG		PG		GLY	
		Max. Solub., M	Apparent Viscosity	Max. Solub., M	Apparent Viscosity	Max. Solub., M	Apparent Viscosity	Max. Solub., M	Apparent Viscosity	Max. Solub., M	Apparent Viscosity	Max. Solub., M	Apparent Viscosity
1	No Surfactant	<i>n.a.</i>	●●	<i>n.a.</i>	●●	<i>n.a.</i>	●●●	<i>n.a.</i>	●	<i>n.a.</i>	●	<i>n.a.</i>	●●●
2	Cetyltrimethylammonium Bromide	0.124	●●	0.11	●●	0.016	●●●	0.079	●●	0.101	●●	0.065	●●●
3	<i>p</i> -dodecyloxybenzyltrimethylammonium bromide	0.37	●●	0.232	●●	0.116	●●●	0.384	●●	0.205	●●	0.33	●●●
4	<i>p</i> -octyloxybenzyltriethylammonium bromide	2.66	●●	2.02	●●	0.5	●●●	1.184	●●	0.824	●●	0.5	●●●
5	<i>p</i> -dodecyloxybenzyl dimethylamine N-oxide	0.025	●●●	0.199	●●●●	0.067	●●●●	0.163	●●	0.153	●●	0.086	●●●
6	Cetyldimethylethanolammonium bromide	0.023	●●	0.127	●●●●	0.043	●●●	0.127	●●	0.127	●●	0.13	●●●
7	Cetylmethyldiethanolammonium methanesulfonate	0.12	●●	0.24	●●●	0.06	●●●●	0.256	●●	0.252	●●	0.28	●●●●
8	Cetyltriethanolammonium bromide	0.026	●●●	0.042	●●●●	0.176	●●●●	0.022	●●	0.059	●●	0.15	●●●
9	Cetyldiethanolamine N-oxide	0.014	●●●●●	0.145	●●	0.026	●●●●	0.156	●●	0.142	●●	0.15	●●●●
10	<i>p</i> -dodecyloxybenzyl dimethylethanolammonium bromide	0.11	●●	0.11	●●	0.033	●●●	0.179	●●	0.179	●●	0.03	●●●
11	Didodecylmethylethanolammonium bromide	0.176	●●	0.176	●●	0.09	●●●	0.183	●●	0.183	●●	0.1	●●●
12	Didodecylmethylethanolammonium chloride	0.156	●●	0.118	●●	0.029	●●●	0.156	●●	0.178	●●	0.034	●●●
13	N,N-dimethyl-N-hexadecyl-(D)-glucammonium methanesulfonate	0.118	●●	0.12	●●	0.012	●●●●	0.035	●●	0.115	●●	0.01	●●

The solubilities of the amphiphiles were all in the same order of magnitude (about 0.1 M), except for cetyltrimethylammonium bromide (Entry 2) that showed a slight lower solubility in all the samples and *p*-octyloxybenzyltriethylammonium bromide (Entry 4) that showed a slightly higher maximum solubility.

Regarding the apparent viscosity, without any added surfactant (Entry 1), the liquids showed very high fluidity (DEG, PG) or had a slight viscosity (ChCl/DEG, ChCl/PG); Glycerol and glycerol-based DES (ChCl/GLY) had a slightly lower fluidity. The surfactants showed similar trends in the different DESs liquids, only slight differences were observed from one DES to another with the same amphiphile. Cetyltrimethylammonium Bromide (Entry 2) did not provoke any significant change in the fluidity of the liquids as expected because it is not a gelator surfactant but is the model cationic amphiphile in the set. *p*-alkyloxybenzyl-surfactants (Entries 3 and 4) didn't induce significant increase in the viscosity of the mixtures even if it is known they can act as gelators in water.³⁷ Ethanol-headed surfactants (Entries 6-13), on the contrary, showed significant changes in the fluidity of the DESs mixtures, in particular in those (Entries 5 and 9) where, combined to the ethanol groups, N-oxide functions are present in the headgroup. Cetyldiethanolamine N-oxide (Entry 9) in ChCl/DEG solution (Figure 1) was the only surfactant in the whole set that showed a really high increase in the viscosity of the DES and its solution did not flow down in the tube inversion test.⁴¹

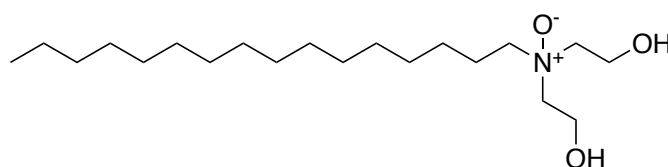


Figure 1. Cetyldiethanolamine N-oxide structure.

The introduction of a *p*-alkyloxybenzyl- as hydrophobic portion in the N-oxide (i.e. *p*-dodecyloxybenzyltrimethylamine N-oxide, entry 5) did not increase the viscosity of the mixtures, suggesting a more relevant role of the headgroup of the surfactant in the process. In particular, the hydrogen bonds that can occur between the alcoholic residues, and the H-bond based interactions of

the DESs and the H-bond acceptor site represented by the N-oxide, seem to have a relevant role in determining the solvo-philic interactions of the headgroup with the solvent as well as a head-head interactions between the surfactants that usually favours the gelification process in water.⁴⁵ Charged headgroups of the surfactants, in fact, (Entries 2-5, 7-8, 10-13) seemed not to favour the reduction of the fluidity of the system probably as they can have a lower affinity with the structured solvents. However, as cetyldiethanolamine N-oxide showed firm solutions in the tube inversion test only with ChCl/DEG DES but lower viscosity with the other liquids, it was necessary to expand the investigation on other DESs liquids, in order to find any other candidates to form gel phases. To this aim, the gelling ability of cetyldiethanolamine N-oxide was probed in a wide range of DES, as reported in Figure 2. The DES considered differ both in the hydrogen bond donor (HBD) and the hydrogen bond acceptor (HBA).

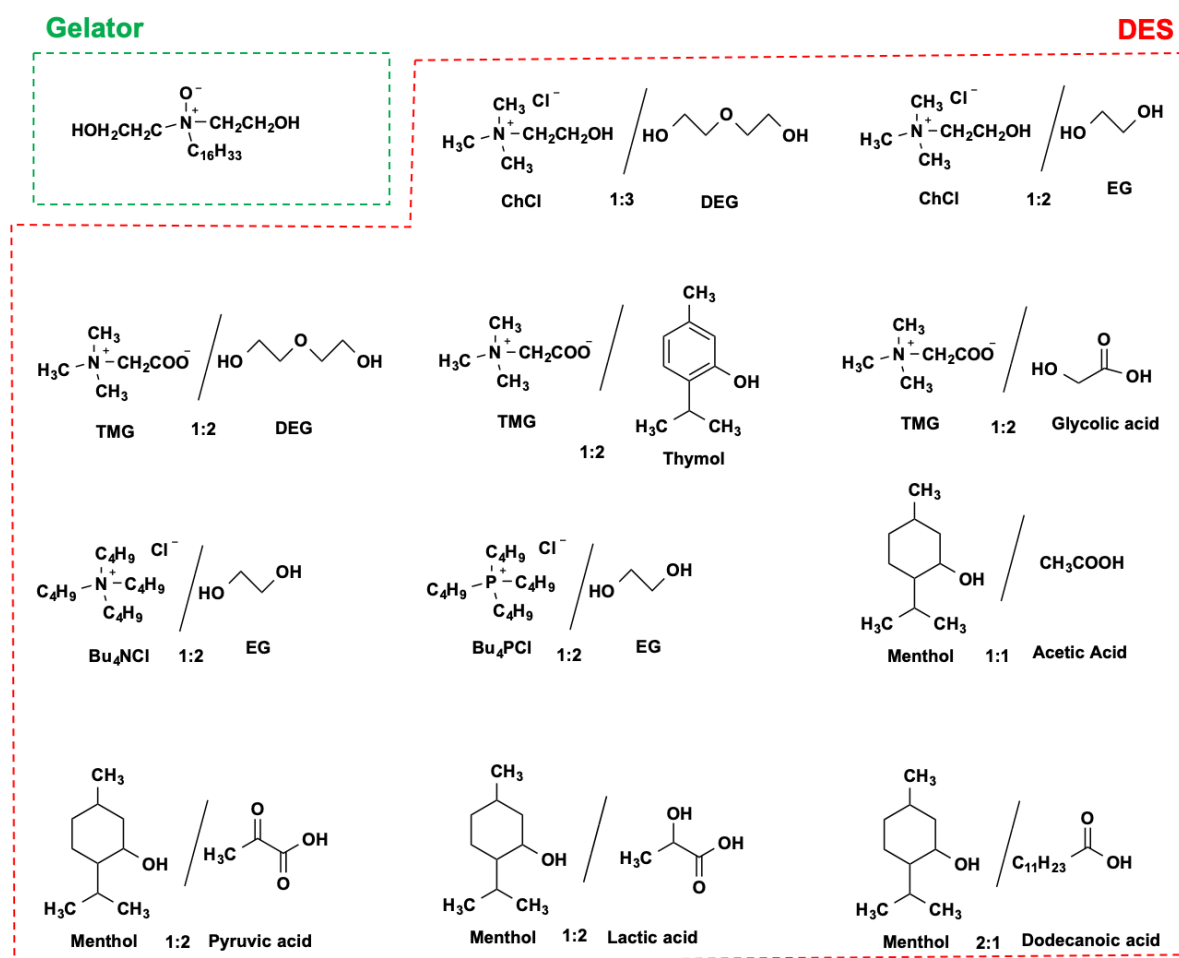


Figure 2. Gelator and DESs considered for gelation tests.

In particular, HBD range from a phenol, to diols and carboxylic acids, whereas the HBA used comprise ammonium and phosphonium salts, together with a betaine and an alcohol. To assess the ability of the surfactant to harden these DESs, variable amounts of surfactants and DES were weighed in a screw-capped vial and the mixture was heated to a suitable temperature. When complete dissolution of the surfactant was observed, the solution obtained was left to stand at room temperature overnight. All the samples were heated at 60 °C for 1 h, with the only exception of the ones in TMG/GA, for which a temperature of 90 °C was required to achieve complete dissolution. Then, gel formation was assessed by the tube inversion method.⁴¹ When a gel was obtained, we carried out gelation tests at decreasing concentration of surfactant, to determine the critical gelation concentration (CGC), *i.e.* the minimum gelator concentration at which a gel forms. The results of these tests are reported in Table 2.

Table 2. Gelation tests, concentration range explored, CGCs and T_{gel} at 5 wt%. Unless otherwise stated, the HBA/HBD molar ration in DES is 1/2.

DES	Range (wt%)	App. ^b	CGC (wt%)	T_{gel} (°C) ^c
ChCl/DEG 1/3	0.5-5	OG	0.8	48
TMG/DEG	0.5-8	OG	3.9	43
TMG/GA ^a	0.25-9	TG	0.9	32
TMG/Thy	0.5-10	S		
ChCl/EG	1-5	OG	1.9	47
Bu ₄ NCl/EG	1-7	S		
Bu ₄ PCI/EG	1-5	S		
Ment/HOAc 1/1	1-7	S		
Ment/Pyr	1-7	S		
Ment/Lac	1-7	S		
Ment/Dodec 2/1	1-7	S		

[a] Mixture heated at 90 °C. [b] S: soluble; OG: opaque gel; TG: translucent gel. [c] T_{gel} determined at 5 wt%. T_{gel} values are reproducible within $\pm 1^\circ\text{C}$.

Looking at the results reported in Table 2, we can infer that gels were obtained only in DES composed by a glycol as HBD and ChCl or TMG as HBA. Notably, the solubility of the surfactant was too high to form a gel in all the other cases. Indeed, substituting ChCl with tetrabutylphosphonium or tetrabutylammonium salts, the samples always resulted as clear solutions. Moreover, no gelation was observed in more hydrophobic DES, such as the menthol-based ones, in which once again, the gelation tests only gave rise to clear solutions. Representative pictures of the gels are reported in Figure 3.

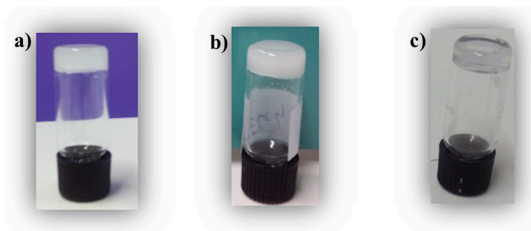


Figure 3. Representative pictures 5 wt% eutectogels formed in of a) ChCl/DEG, b) TMG/DEG and c) TMG/GA.

The trend of CGCs observed gives a useful comparison of the propensity of DES to support gelation. In particular, CGC increased following the order $\text{ChCl/DEG} \approx \text{TMG/GA} < \text{ChCl/EG} < \text{TMG/DEG}$. Comparing the CGCs observed in ChCl/DEG and ChCl/EG can shed light on the effect of the nature of the HBD on the ability of the solvent to support gelation, showing that a smaller HBA, such as EG compared to DEG, allows gelation to take place at a much lower concentration of gelator. Analogously, comparing the CGC of gels obtained in DES differing for HBA, such as ChCl/DEG and TMG/DEG, evidences that the former is a more favorable solvent for gelation. Both these results suggest that DES with a stronger H-bonding between the components are more favourable solvents for gelation. Indeed, it is reported that, HBA being the same, the strength of H-bonding increases with the number of oxymethylene units in the diols.⁴⁶ Similarly, in the case of the gels formed in ChCl/DEG and TMG/DEG, gelation is favored in the former, in which the hydrogen bond acceptor bears the chloride anion, with a higher charge density compared to the carboxylate unit in TMG. Then, to assess the thermal stability of the gels, we determined the gel-sol transition temperature, T_{gel} , at a common gelator concentration, 5 wt%. To have a meaningful comparison, from now on all the discussion will refer to 5 wt% gels.

Results collected show that in the case of ChCl-based gels, T_{gel} is not affected by the nature of the HBD. However, changing the HBA from ChCl to TMG causes a significant decrease in T_{gel} , according to the higher charge density in the chloride anion compared with the carboxylate (TMG). Finally, for TMG-based gels, the presence of a stronger HBD gives rise to a feebler gel. Probably, in

the latter case, stronger HBA-HBD interaction within the solvent makes more difficult the establishment of the gelator-DES interactions, required to stabilize the gel network.

3.1 Gelation kinetics by Opacity Measurements

To further characterize the eutectogels, we investigated the gelation kinetics by time-dependent opacity investigations carried out by UV-vis spectroscopy. In this case, the absorbance measured is related to the crystallinity of the gel and to occurrence of polydispersity.⁴⁷ Accordingly, this methodology has been applied to probe the gelation kinetics in opaque hydrogels,⁴⁸ organogels^{49,50} and ionic liquid gels.^{51,52}

In this case, we were able to follow the opacity as a function of time for all gels, with the exception of the one in TMG/GA, due to its translucent nature. Plots of absorbance as a function of time obtained are reported in Figure 4.

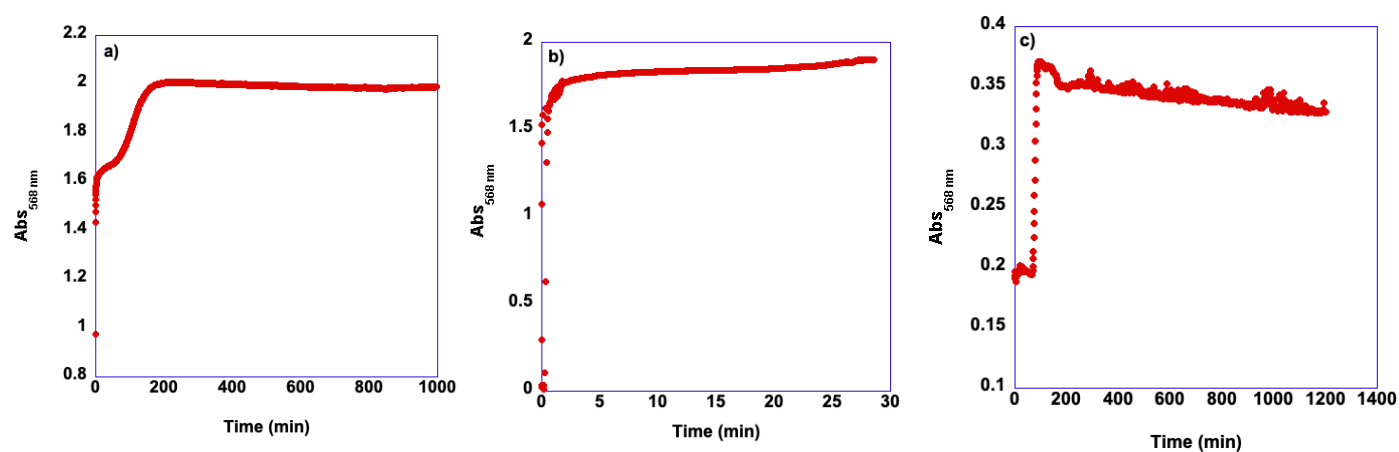


Figure 4. Opacity measurements for gelation of surfactant in a) ChCl/DEG, b) ChCl/EG and c) TMG/DEG.

Looking at the plots reported in Figure 4, shows that ChCl/EG is the fastest forming gels, with plateau times amounting to 5, 200 and 300 min for ChCl/EG, ChCl/DEG and TMG/DEG, respectively. More specifically, the differences in gelation rate appear larger when comparing the gels formed in DES sharing the same HBA (ChCl/EG and ChCl/DEG) as opposed to what happens for the gels in DES

sharing the same HBD, such as ChCl/DEG and TMG/DEG. In other words, changing the HBD has a much more significant effect on gelation rate compared with the HBA.

Furthermore, plateau absorbances clearly show that the gel formed in TMG/DEG has a lower degree of crystallinity and polydispersity compared with the ones obtained in ChCl/EG and ChCl/DEG. Finally, the plots reported in Figure 4a and 4c show the occurrence of a two-step gelation pathway. The only exception is represented by the gel formed in ChCl/EG, Figure 4b, seems to form with a single step-mechanism. However, due to the fast gelation, it is likely that the first step is so fast that it is not appreciable by this method. Interestingly, these results show a marked difference with the gelation kinetics of amino acid-based eutectogels, probed by opacity measurements, which follow a single step mechanism.^{27,53}

3.2 Rheology measurements

To gain insight into the mechanical properties of our eutectogels and confirm their gel nature, we conducted strain- and frequency sweeps measurements, at 25 °C. In particular, in these experiments the variations of the storage modulus G' , accounting for elastic response of the material, and G'' , related to viscous behavior, are followed as a function of applied strain or frequency. In strain sweep measurements typical gels show $G' > G''$ until a certain strain at which the gel is broken and G'' prevails. The strain at which $G' = G''$, known as crossover point (γ_c), represents the maximum strain to which the gel can be subjected without breaking.

In frequency sweep measurements, a rheological hallmark of gels is their almost constant values over a relatively wide range of frequencies.⁵⁴ Another important parameter that can be extracted from these rheological measurements is the ratio G''/G' , known as $\tan\delta$, which is related to the strength of colloidal interactions within the gel phase. We carried out the rheological measurements for all gels, with the exception of the one in ChCl/EG, which was too weak and broke down immediately under the conditions of the experiments. Representative plots of strain and frequency sweeps measurements

for the gel in ChCl/DEG are reported in Figure 5, while the other ones are reported in Figure A.1. The values of the rheological parameters extracted are reported in Table 3.

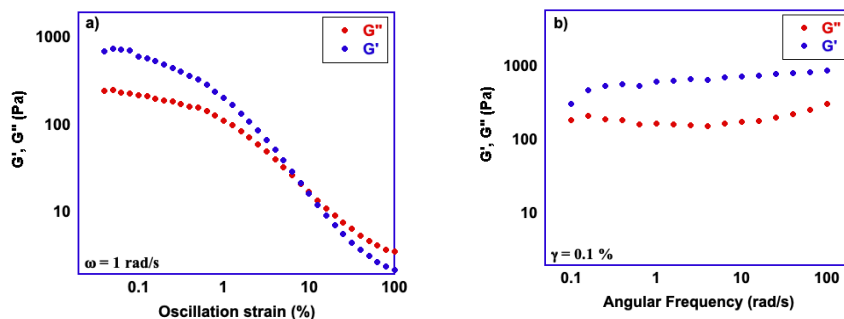


Figure 5. Plots of a) strain and b) frequency sweep measurements for 5 wt% eutectogel in ChCl/DEG.

Table 3. Storage and loss moduli, crossover point and $\tan \delta$ values for 5 wt% eutectogels.

DES	G' (Pa)	G'' (Pa)	γ_c (%)	$\tan \delta$
TMG/DEG	210 ± 20	96 ± 9	17 ± 2	0.46 ± 0.07
ChCl/DEG	640 ± 10	200 ± 40	10.0 ± 0.5	0.33 ± 0.05
TMG/GA	370 ± 90	180 ± 50	20 ± 3	0.51 ± 0.09

Looking at the plots reported in Figure 5 and A.1, shows that in all cases, the trends of moduli as a function of oscillation strain and frequency show the hallmarks of gel-like behaviors. Examination of the values of $\tan \delta$ reported in Table 1 shows that in all cases we observed $\tan \delta < 1$, suggestive of strong colloidal forces underpinning the gel network. In particular, $\tan \delta$ increases along the series ChCl/DEG < TMG/DEG \approx TMG/GA. Consequently, the gel formed in ChCl/DEG is the stiffest one, also in light of its higher G' modulus.

The above trend perfectly recalls the one corresponding to T_{gel} values, indicating that the gel featured by the occurrence of stronger colloidal forces shows higher gel-sol transition temperature. Furthermore, the higher difference between the γ_c values of gels formed in DES differing for the HBA (ChCl/DEG and TMG/DEG) with respect to the ones differing for the HBD (TMG/DEG and

TMG/GA), points out that changing the HBA has the highest impact on the rheological strength of the gels. Finally, both moduli and γ_c are significantly lower than those determined for amino-acid based eutectogels.^{27,53,55}

3.3 Morphology

Morphology of the eutectogels was investigated by SEM images. Each measurement was carried out on samples of the xerogels obtained by washing the gels with ethanol, to remove the deep eutectic solvents. All the xerogels were prepared from 5 wt % eutectogels. The SEM images obtained are reported in Figure 6.

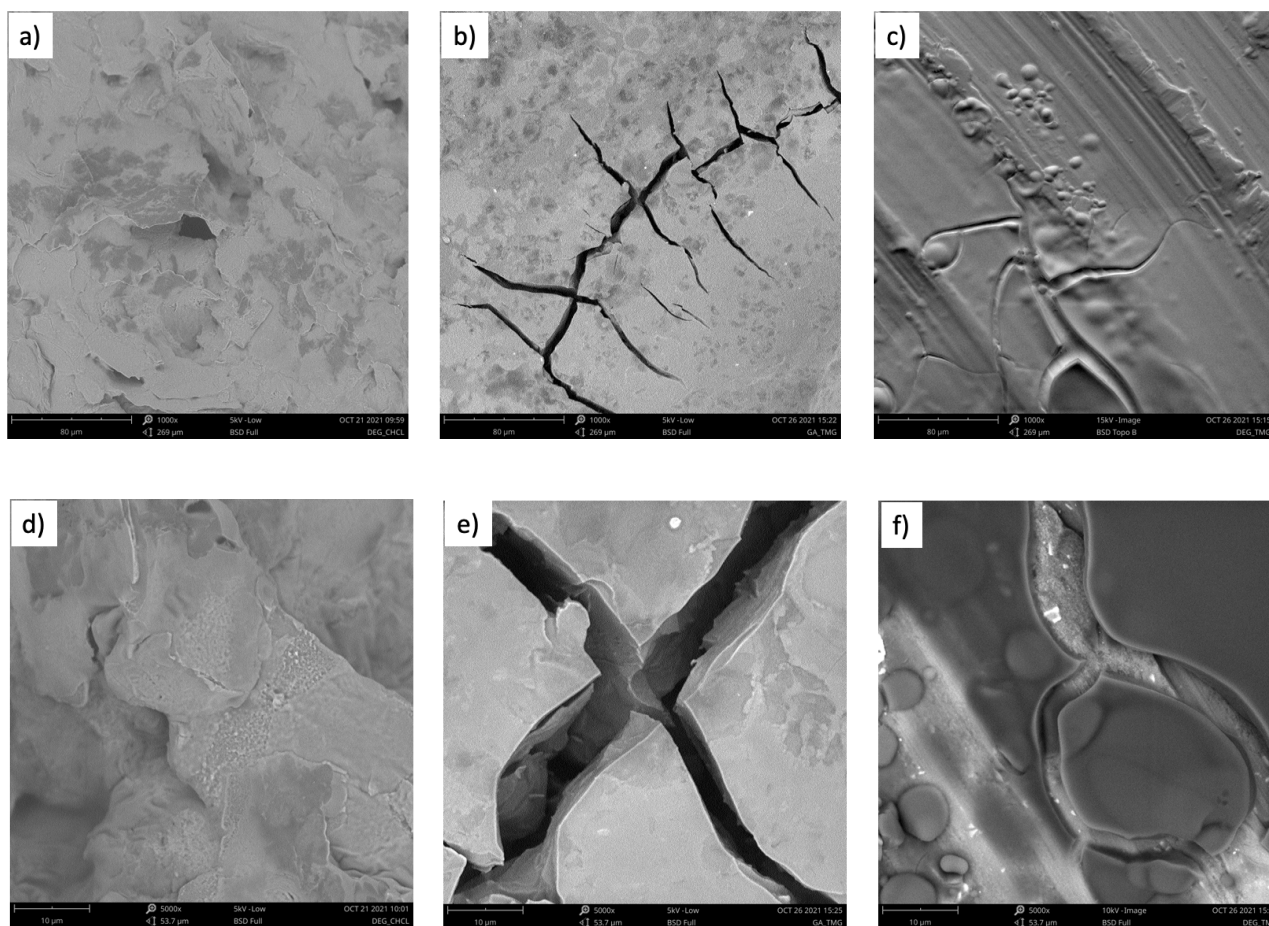


Figure 6. SEM images of xerogels obtained from 5 wt% eutectogels in a) ChCl/DEG (1000X), b) TMG/GA (1000X), c) TMG/DEG (1000X), d) ChCl/DEG (5000X), b) TMG/GA (5000X), c) TMG/DEG (5000X).

Images reported in Figure 6 show different morphologies for each eutectogel although generally they exhibit a compact texture. In particular, the images obtained for the gel in ChCl/DEG (Figures 6a and 6d) show the occurrence of flake-like structures, uniformly distributed in the sample. Conversely, a thicker and more compact texture arise with the gel in TMG/GA (Figures 6b and 6e), for which it is difficult to extract a specific morphology. Finally, the SEM images relevant to the gel obtained in TMG/DEG shows the concomitant presence of spheroidal and elongated structures (Figure 6c and 6f). In particular the image at higher magnification reported in Figure 6f seems to suggest that the elongated object may arise from the further aggregation of the spheroidal ones.

3.4 Iodine adsorption

Having assessed the structural properties of the gels, we tested their ability to remove I₂ from hexane solution. The use of such kind of materials to remove harmful contaminants, appears quite relevant in terms of sustainability, due to the nature of components, which are low impacting in terms of both eco- and biotoxicity. To our aim, we firstly evaluated the stability of each gel towards the contact with the solvent. Consequently, we placed 500 μL of hexane onto 250 mg of each gel, at 5 wt%, keeping the two phases in contact for 24 h at 25 °C. After this treatment, all the gels were unaltered, as evaluated by tube inversion test,⁴¹ with the exception of the one formed in ChCl/EG, which partially collapsed, in agreement with its lower mechanical resistance shown by rheology. Subsequently, for the gels that resisted to contact with the organic solvent, we wanted to ascertain whether any gel component was released in the organic phase as a result of contact. To this aim, we placed 500 μL of deuterated cyclohexane on top of 250 mg of each gel, once again maintaining contact for 24 h at 25 °C. Then, we removed the organic phase and recorded the ¹H NMR spectrum using DMSO as internal standard. The spectra obtained are reported in Figure A.2.

The spectra reported in Figure A.2 show a very limited release of DES component in the case of the gel in TMG/DEG, amounting to 0.3% of TMG while for the other gels no significant release of DES components in the organic phase occurred. In every case, we found no evidence for release of

surfactant either. In the light of this, we carried out adsorption experiments by contacting each gel (500 mg) with 1 mL of a 500 ppm solution of I₂ in *n*-hexane, at 25 °C. After a suitable time, the organic phase was removed and the UV-vis spectrum was recorded. Then, we determined the removal efficiency by means of Equation 1

$$RE (\%) = \frac{C_i - C_t}{C_i} \cdot 100 \quad (1)$$

where C_i is the initial concentration of I₂ and C_t is the residual I₂ concentration after the time (t), based on a calibration curve previously determined. In Figure 7, we report the RE values determined for each gel after contact times of 5 and 30 minutes.

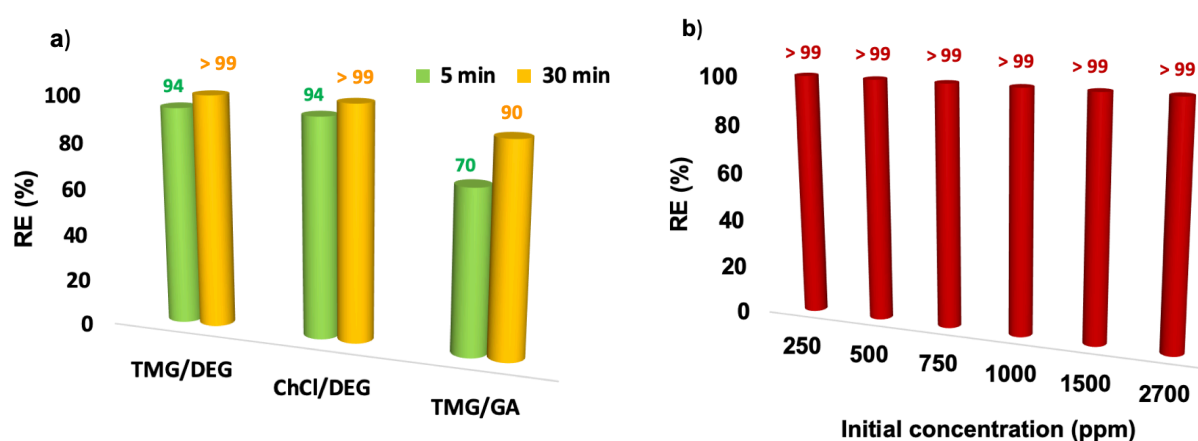


Figure 7. a) Plot of removal efficiency of iodine by 5 wt% eutectogels after 5 and 30 minutes of contact, at 25 °C. b) Removal efficiency of gel in ChCl/DEG at different initial I₂ concentrations. RE% are reproducible within 3%, based on triplicate experiments.

In general, the adsorption is quite fast and, in most cases, a practically quantitative removal was achieved after only 5 minutes. Only the gel formed in TMG/GA displayed a slightly slower adsorption of iodine with RE after 5 minutes amounting to 70%, as compared with more than 90% for the other gels. Given the encouraging results obtained, we wanted to investigate if this efficient removal is

maintained over a wider range of initial iodine concentrations. To this aim, we carried out the same adsorption experiment, using the gel formed in ChCl/DEG and iodine solution in hexane with concentrations ranging from 250 to 2700 ppm and contact times of 30 minutes. This gel was chosen on the grounds of the fast adsorption and negligible release of DES components in the hexane phase. Furthermore, as above stated, it showed the highest T_{gel} (Table 2) and stiffness (Table 3).

The results reported in Figure 7b clearly show that the eutectogel formed in ChCl/DEG provided fast and thorough removal of iodine from the organic phase even when the initial concentration increased to 2700 ppm, showing no saturation. On the other hand, even for the lowest concentration, 250 ppm, 30 minutes were sufficient to achieve practically total removal of iodine from the hexane solution.

The good performance of the eutectogel in I_2 removal can result from the action of two concomitant factors. The first one is clearly the ability of the contaminant to distribute between organic and gel phase. Results obtained clearly show the higher ability of the eutectogel to trap the target species. However, the adsorption efficiency can also positively feel the presence of a permanent dipole in the gelator structure. This could induce the formation of a dipole in the I_2 molecule, driving the adsorption process as a consequence of the occurrence of dipole-dipole interactions.

With the above results in hand, we investigated if the same gel could be reused for further iodine adsorption. Towards this aim, after a time of contact of the gel with the iodine solution, under the same experimental conditions described, we removed the organic phase and replaced it with a fresh batch of iodine solution. The results obtained are summarized in Figure 8a.

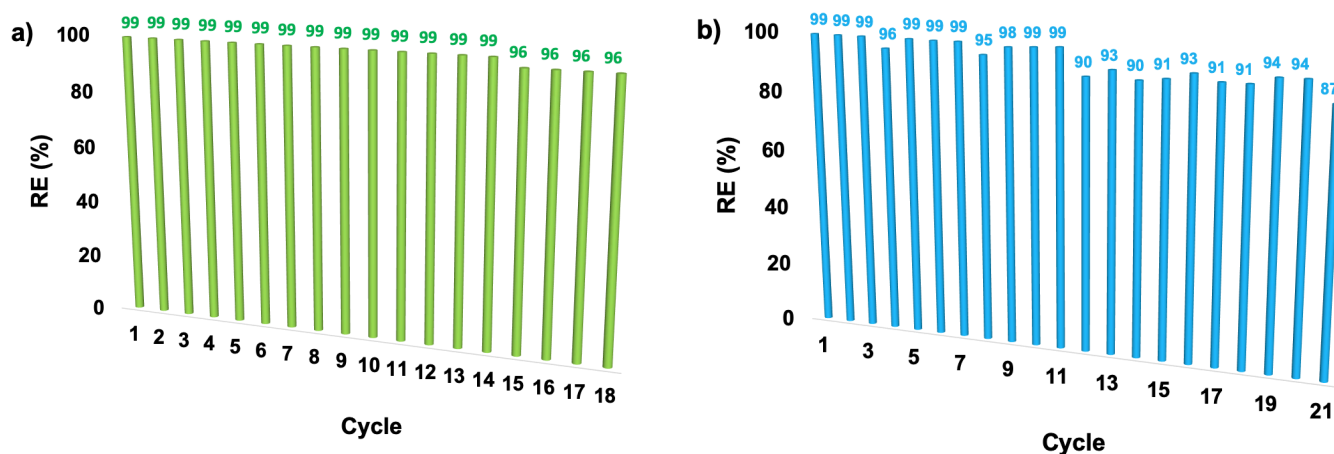


Figure 8. Plots of a) removal efficiency of iodine by ChCl/DEG eutectogel (5 wt %) and b) after regeneration of the I₂-laden gel, at 25 °C, after 30 minutes. RE% are reproducible within 3%, based on triplicate experiments.

The results reported in Figure 8a show that eutectogel in ChCl/DEG maintained its removal efficiency over 18 cycles, after which, however a partial collapse of the gel occurred. The gel could be restored by heating at 60 °C for 1 hour and keeping it at room temperature overnight. The restored gel was then washed with portions of 2-methyltetrahydrofuran (3 X 0.5 mL). This solvent was chosen on the grounds of the stability shown by the eutectogel upon contact. Moreover, it also allows to perform the regeneration of the adsorbent paying attention to the environmental impact of the process, since this solvent can be obtained from renewable sources and it is one of the solvent proposed by solvent selection guides of Green Chemistry.⁵⁶

The amount of iodine recovered was determined spectrophotometrically, showing that 83% of the iodine adsorbed could be removed from the gel. This gel was then reused for further adsorption runs, as reported in Figure 8b. As reported in Figure 8b, the gel kept its efficiency as sorbent, showing a slight loss in performance at the 13th cycle and another after 20 reuses. However, the removal efficiency still retained high values, highlighting the high recyclability degree of this gel.

Finally, to gain information on the maximum adsorption capacity of the eutectogel, and to have insight on the adsorption mechanism, we carried out experiments in the presence of different amounts

of iodine in the hexane solutions. To ensure that an equilibrium is reached, the contact time was extended to 6 h, at 25 °C. After each experiment, we calculated the equilibrium adsorption capacity, Q_e , which is the mass of iodine adsorbed in mg, per gram of gel. Then, we plotted Q_e as a function of C_e , the equilibrium concentration of I_2 expressed in mg/L, obtaining the plot reported in Figure 9.

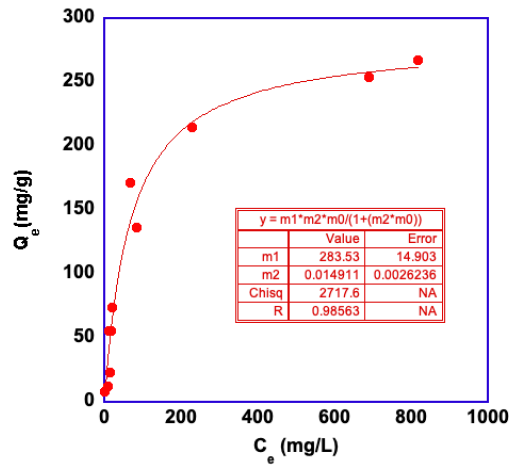


Figure 9. Plot of equilibrium adsorption efficiency for 5 wt% eutectogel in ChCl/DEG as a function of equilibrium I_2 concentration, at 25 °C. Non-linear fitting according to Langmuir isotherm model.

The plot of Q_e as a function of C_e describes a typical hyperbolic trend. To obtain mechanistic insight on the adsorption process, we fitted the curve according to two of the most widely accepted adsorption models, namely the Langmuir⁵⁷ and the Freundlich isotherm.^{58,59} In particular, the Langmuir model assumes monolayer coverage of the adsorbate on the surface of the gel, which is treated as homogeneous. According to this model Q_e is expressed by Equation 2

$$Q_e = \frac{K_L * Q_{max} * C_e}{1 + K_L * C_e} \quad (2)$$

where Q_{\max} is the maximum adsorption capacity and K_L is the Langmuir constant. On the other hand, the Freundlich model is based in multilayer adsorption, and treats the surface of the adsorbent as heterogeneous. According to this model, Q_e can be expressed by Equation 3, reported below

$$Q_e = K_F * (C_e)^{1/n} \quad (3)$$

where K_F is the Freundlich constant, and is the adsorption intensity. The results of the non-linear fitting based on the two models are summarized in Table 4.

Table 4. Results of non-linear fitting according to mono- and multilayer adsorption models.

Langmuir			Freundlich		
Q_{\max} (mg/g)	K_L	R^2	K_F	$1/n$	R^2
280 ± 15	$(1.5 \pm 0.3) \cdot 10^{-2}$	0.970	25 ± 7	0.36 ± 0.05	0.906

The results reported in Table 4 clearly show that the Langmuir model is the most suitable to describe the adsorption process. Consequently, we can infer that the maximum adsorption capacity of the eutectogel formed in ChCl/DEG is 280 mg/g.

To further assess the performance of our eutectogel in iodine capture from solution, we compared our results with other ones reported in the literature for the same purpose. In particular, we focused on gel-based sorbent systems, either polymeric or supramolecular. The results of the selected systems, together with those obtained in the present work, are reported in Table 5.

Table 5. Time of contact and adsorption capacity of I₂-removing gels described in the literature and in this work.

Entry	Sorbent	Time of contact (h)	Solvent	Q _{max} (mg/g)
1	Eutectogel ^a	6	Hexane	280
2	Metallogel ⁶⁰	24	Petroleum ether	303
3	Aerogel ⁶¹	24	Hexane	234
4	Xerogel ⁶²	3	Water	490
5	Xerogel ⁶³	1.5	Hexane	1800
6	Hybrid gel ⁶⁴	16	Hexane	2950

[a] This work.

Looking at the results reported in Table 5, highlights that the performance of our eutectogel is comparable or superior to that of a coordination polymer metallogel⁶⁰ and of a polymer-based aerogel,⁶¹ with the further advantage of requiring a much lower contact time between the adsorbent and the apolar solvent solution of iodine (entries 1-3). Furthermore, despite the simplicity of the components, the performance of our eutectogel is only slightly inferior to the one of the macrocycle-based xerogel described by Li et al.,⁶² both in terms of contact time and adsorption capacity, remembering that adsorption was carried out toward iodine dissolved in different solvents (entries 1 and 4). In the remaining cases, the performance of our gels in terms of adsorption capacity is lower than that of polymer⁶³ or multicomponent hybrid gels⁶⁴ (entries 1,5-6). However, our eutectogel still retains the advantage of simplicity of components and shorter contact time.

Overall, these comparisons show that the supramolecular eutectogels described in this work are simple, but effective nanostructured sorbents achieving fast and thorough adsorption of iodine, from apolar solvents solutions.

5. Conclusions

In this work, we described the preparation and characterization of surfactant-based supramolecular eutectogels and investigated their performance as sorbents for the removal of iodine from apolar

solvent solutions. Firstly, we conducted a screening of several amphiphiles, finding that cetyldiethanolamine N-oxide was the best candidate. Gelation tests revealed that this amphiphile can harden different DESs, allowing the obtainment of some eutectogels based on components with low bio- and environmental impact. Gel phases obtained display good to high thermal stability, with T_{gel} higher than 40 °C for most cases. Investigation of gelation kinetics by RLS and opacity measurements, showed that these gels formed through a two-step process. Both T_{gel} and rheological properties of the eutectogels show a pronounced effect of the HBA. In particular, a stronger HBA gives rise to the formation of eutectogels with higher stiffness and T_{gel} .

Our eutectogels can be used as sorbents for the removal of contaminants, working at room temperature and ambient pressure they allowed fast and thorough removal of iodine from solutions in apolar solvents. In particular, the best performing one, formed in ChCl/DEG, maintained high removal efficiency over a wide range of initial iodine concentrations. Adsorption could be described by the Langmuir isotherm and the maximum adsorption capacity Q_{max} amounted to 280 mg/g. It can be reused for at least 18 cycles, regenerated by washing with a solvent recommended by solvent selection guide based on Green Chemistry and reused for further 20 cycles without loss in performance. Furthermore, from a sustainability point of view, they show the advantage of being performed by components with good eco- and biocompatibility, reducing the impact of the adsorbent material at the time of its disposal.

Acknowledgements

We thank University of Palermo for financial support (FFR 2020-D'Anna and FFR 2020-Marullo).

Author contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of interest

The authors declare no competing financial interest.

References

- (1) Soelberg, N. R.; Garn, T. G.; Greenhalgh, M. R.; Law, J. D.; Jubin, R.; Strachan, D. M.; Thallapally, P. K. Radioactive Iodine and Krypton Control for Nuclear Fuel Reprocessing Facilities. *Sci. Technol. Nucl. Install.* **2013**, *2013*, 702496, DOI: 10.1155/2013/702496.
- (2) Hormann, V.; Fischer, H. W. A Simple Compartment Model for the Dynamical Behavior of Medically Derived ¹³¹I in a Municipal Wastewater Treatment Plant. *Environ. Sci. Technol.* **2018**, *52*, 9235-9242, DOI: 10.1021/acs.est.8b01553.
- (3) Saiz-Lopez, A.; Plane, J. M. C.; Baker, A. R.; Carpenter, L. J.; von Glasow, R.; Gómez Martín, J. C.; McFiggans, G.; Saunders, R. W. Atmospheric Chemistry of Iodine. *Chem. Rev.* **2012**, *112*, 1773-1804, DOI: 10.1021/cr200029u.
- (4) Nandanwar, S. U.; Coldsnow, K.; Utgikar, V.; Sabharwall, P.; Eric Aston, D. Capture of harmful radioactive contaminants from off-gas stream using porous solid sorbents for clean environment – A review. *Chem. Eng. J.* **2016**, *306*, 369-381, DOI: 10.1016/j.cej.2016.07.073.
- (5) Vellingiri, K.; Kim, K.-H.; Pournara, A.; Deep, A. Towards high-efficiency sorptive capture of radionuclides in solution and gas. *Prog. Mater. Sci.* **2018**, *94*, 1-67, DOI: 10.1016/j.pmatsci.2018.01.002.
- (6) Sophia, C.; Lima, E. C. Removal of emerging contaminants from the environment by adsorption. *Ecotoxicol. Environ. Safety* **2018**, *150*, 1-17, DOI: 10.1016/j.ecoenv.2017.12.026.
- (7) Jiménez-Reyes, M.; Almazán-Sánchez, P. T.; Solache-Ríos, M. Radioactive waste treatments by using zeolites. A short review. *J. Environ. Radioact.* **2021**, *233*, 106610, DOI: 10.1016/j.jenvrad.2021.106610.
- (8) Riley, B. J.; Chun, J.; Um, W.; Lepry, W. C.; Matyas, J.; Olszta, M. J.; Li, X.; Polychronopoulou, K.; Kanatzidis, M. G. Chalcogen-Based Aerogels As Sorbents for Radionuclide Remediation. *Environ. Sci. Technol.* **2013**, *47*, 7540-7547, DOI: 10.1021/es400595z.
- (9) Riley, B. J.; Chong, S. Environmental Remediation with Functional Aerogels and Xerogels. *Global Challenges* **2020**, *4*, 2000013, DOI: 10.1002/gch2.202000013.
- (10) Alahabadi, A.; Singh, P.; Raizada, P.; Anastopoulos, I.; Sivamani, S.; Dotto, G. L.; Landarani, M.; Ivanets, A.; Kyzas, G. Z.; Hosseini-Bandegharaei, A. Activated carbon from wood wastes for the removal of uranium and thorium ions through modification with mineral acid. *Colloids Surf., A* **2020**, *607*, 125516, DOI: 10.1016/j.colsurfa.2020.125516.
- (11) Karkeh-abadi, F.; Saber-Samandari, S.; Saber-Samandari, S. The impact of functionalized CNT in the network of sodium alginate-based nanocomposite beads on the removal of Co(II) ions from aqueous solutions. *J. Hazard. Mater.* **2016**, *312*, 224-233, DOI: 10.1016/j.jhazmat.2016.03.074.
- (12) Hu, R.; Shao, D.; Wang, X. Graphene oxide/polypyrrole composites for highly selective enrichment of U(VI) from aqueous solutions. *Polym. Chem.* **2014**, *5*, 6207-6215, DOI: 10.1039/C4PY00743C.
- (13) Patra, K.; Ansari, S. A.; Mohapatra, P. K. Metal-organic frameworks as superior porous adsorbents for radionuclide sequestration: Current status and perspectives. *J. Chromatogr. A* **2021**, *1655*, 462491, DOI: 10.1016/j.chroma.2021.462491.

- (14) Zhong, X.; Liang, W.; Wang, H.; Xue, C.; Hu, B. Aluminum-based metal-organic frameworks (CAU-1) highly efficient UO₂²⁺ and TcO₄⁻ ions immobilization from aqueous solution. *J. Hazard. Mater.* **2021**, *407*, 124729, DOI: 10.1016/j.jhazmat.2020.124729.
- (15) Sava, D. F.; Garino, T. J.; Nenoff, T. M. Iodine Confinement into Metal–Organic Frameworks (MOFs): Low-Temperature Sintering Glasses To Form Novel Glass Composite Material (GCM) Alternative Waste Forms. *Ind. Chem. Eng. Res.* **2012**, *51*, 614-620, DOI: 10.1021/ie200248g.
- (16) Demir, S.; Brune, N. K.; Van Humbeck, J. F.; Mason, J. A.; Plakhova, T. V.; Wang, S.; Tian, G.; Minasian, S. G.; Tylliszczak, T.; Yaita, T.; Kobayashi, T.; Kalmykov, S. N.; Shiwaku, H.; Shuh, D. K.; Long, J. R. Extraction of Lanthanide and Actinide Ions from Aqueous Mixtures Using a Carboxylic Acid-Functionalized Porous Aromatic Framework. *ACS Cent. Sci.* **2016**, *2*, 253-265, DOI: 10.1021/acscentsci.6b00066.
- (17) Amabilino, D. B.; Smith, D. K.; Steed, J. W. Supramolecular materials. *Chem. Soc. Rev.* **2017**, *46*, 2404-2420, DOI: 10.1039/C7CS00163K.
- (18) Draper, E. R.; Adams, D. J. Low-Molecular-Weight Gels: The State of the Art. *Chem* **2017**, *3*, 390-410, DOI: 10.1016/j.chempr.2017.07.012.
- (19) Weiss, R. G. The Past, Present, and Future of Molecular Gels. What Is the Status of the Field, and Where Is It Going? *J. Am. Chem. Soc.* **2014**, *136*, 7519-7530, DOI: 10.1021/ja503363v.
- (20) Cringoli, M. C.; Marchesan, S.; Melchionna, M.; Fornasiero, P. Nanostructured Gels for Energy and Environmental Applications. *Molecules* **2020**, *25*, 5620, DOI: 10.3390/molecules25235620.
- (21) Okesola, B. O.; Smith, D. K. Applying low-molecular weight supramolecular gelators in an environmental setting – self-assembled gels as smart materials for pollutant removal. *Chem. Soc. Rev.* **2016**, *45*, 4226-4251, DOI: 10.1039/C6CS00124F.
- (22) Marr, P. C.; Marr, A. C. Ionic liquid gel materials: applications in green and sustainable chemistry. *Green Chem.* **2016**, *18*, 105-128, DOI: 10.1039/C5GC02277K.
- (23) Alonso, D. A.; Baeza, A.; Chinchilla, R.; Guillena, G.; Pastor, I. M.; Ramón, D. J. Deep Eutectic Solvents: The Organic Reaction Medium of the Century. *Eur. J. Org. Chem.* **2016**, *2016*, 612-632, DOI: <https://doi.org/10.1002/ejoc.201501197>.
- (24) Paiva, A.; Craveiro, R.; Aroso, I.; Martins, M.; Reis, R. L.; Duarte, A. R. C. Natural Deep Eutectic Solvents – Solvents for the 21st Century. *ACS Sustainable Chem. Eng.* **2014**, *2*, 1063-1071, DOI: 10.1021/sc500096j.
- (25) Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060-11082, DOI: 10.1021/cr300162p.
- (26) Tomé, L. C.; Mecerreyes, D. Emerging Ionic Soft Materials Based on Deep Eutectic Solvents. *J. Phys. Chem. A* **2020**, *124*, 8465-8478, DOI: 10.1021/acs.jpca.0c04769.
- (27) Marullo, S.; Meli, A.; Dintcheva, N. T.; Infurna, G.; Rizzo, C.; D'Anna, F. Environmentally Friendly Eutectogels Comprising l-amino Acids and Deep Eutectic Solvents: Efficient Materials for Wastewater Treatment. *ChemPlusChem* **2020**, *85*, 301-311, DOI: 10.1002/cplu.202000017.
- (28) Rizzo, C.; Marullo, S.; Campodonico, P. R.; Pibiri, I.; Dintcheva, N. T.; Noto, R.; Millan, D.; D'Anna, F. Self-Sustaining Supramolecular Ionic Liquid Gels for Dye Adsorption. *ACS Sustainable Chem. Eng.* **2018**, *6*, 12453-12462, DOI: 10.1021/acssuschemeng.8b03002.
- (29) Rizzo, C.; Marullo, S.; D'Anna, F. Carbon-based ionic liquid gels: alternative adsorbents for pharmaceutically active compounds in wastewater. *Environ. Sci.: Nano* **2021**, *8*, 131-145, DOI: 10.1039/D0EN01042A.
- (30) Rizzo, C.; Marullo, S.; Dintcheva, N. T.; D'Anna, F. Carbon Nanomaterial Doped Ionic Liquid Gels for the Removal of Pharmaceutically Active Compounds from Water. *Molecules* **2019**, *24*, 2788, DOI: 10.3390/molecules24152788.
- (31) Rizzo, C.; Andrews, J. L.; Steed, J. W.; D'Anna, F. Carbohydrate-supramolecular gels: Adsorbents for chromium(VI) removal from wastewater. *J. Colloid Interface Sci.* **2019**, *548*, 184-196, DOI: 10.1016/j.jcis.2019.04.034.

- (32) Billeci, F.; D'Anna, F.; Gunaratne, H. Q. N.; Plechkova, N. V.; Seddon, K. R. "Sweet" ionic liquid gels: materials for sweetening of fuels. *Green Chem.* **2018**, *20*, 4260-4276, DOI: 10.1039/C8GC01615A.
- (33) Michaels, E. B. Antimicrobial compositions employing certain substituted alanines and certain t-amine oxides United States of America Patent S4062976A.
- (34) Michaels, E. B. Antimicrobial compositions and methods for utilizing the same employing mixtures of amines United States of America Patent US4107328A.
- (35) Tiecco, M.; Cardinali, G.; Roscini, L.; Germani, R.; Corte, L. Biocidal and inhibitory activity screening of de novo synthesized surfactants against two eukaryotic and two prokaryotic microbial species. *Colloids Surf., B* **2013**, *111*, 407-417, DOI: 10.1016/j.colsurfb.2013.06.033.
- (36) Hoh, G. L. K.; Barlow, D. O.; Chadwick, A. F.; Lake, D. B.; Sheeran, S. R. Hydrogen peroxide oxidation of tertiary amines. *J. Am. Oil Chem. Soc.* **1963**, *40*, 268-271, DOI: 10.1007/BF02633687.
- (37) Brinchi, L.; Germani, R.; Di Profio, P.; Marte, L.; Savelli, G.; Oda, R.; Berti, D. Viscoelastic solutions formed by worm-like micelles of amine oxide surfactant. *J. Colloid Interface Sci.* **2010**, *346*, 100-106, DOI: 10.1016/j.jcis.2010.02.035.
- (38) Brinchi, L.; Germani, R.; Braccalenti, E.; Spreti, N.; Tiecco, M.; Savelli, G. Accelerated decarboxylation of 6-nitrobenzisoazole-3-carboxylate in imidazolium-based ionic liquids and surfactant ionic liquids. *J. Colloid Interface Sci.* **2010**, *348*, 137-145, DOI: 10.1016/j.jcis.2010.04.029.
- (39) Raghavan, S. R.; Cipriano, B. H.: Gel Formation: Phase Diagrams Using Tabletop Rheology and Calorimetry. In *Molecular Gels*; Weiss, R. G., Terech, P., Eds.; Springer: Dordrecht, Netherlands, 2006; pp 241-252.
- (40) Tanaka, J.: Section 2 - Evaluation of gel point. In *Gels Handbook*; Osada, Y., Kajiwara, K., Fushimi, T., Irasa, O., Hirokawa, Y., Matsunaga, T., Shimomura, T., Wang, L., Ishida, H., Eds.; Academic Press: Burlington, 2001; pp 51-64.
- (41) Huang, X.; Raghavan, S. R.; Terech, P.; Weiss, R. G. Distinct Kinetic Pathways Generate Organogel Networks with Contrasting Fractality and Thixotropic Properties. *J. Am. Chem. Soc.* **2006**, *128*, 15341-15352, DOI: 10.1021/ja0657206.
- (42) Takahashi, A.; Sakai, M.; Kato, T. Melting Temperature of Thermally Reversible Gel. VI. Effect of Branching on the Sol-Gel Transition of Polyethylene Gels. *Polym. J.* **1980**, *12*, 335-341, DOI: 10.1295/polymj.12.335.
- (43) Rizzo, C.; Arcudi, F.; Đorđević, L.; Dintcheva, N. T.; Noto, R.; D'Anna, F.; Prato, M. Nitrogen-Doped Carbon Nanodots-Ionogels: Preparation, Characterization, and Radical Scavenging Activity. *ACS Nano* **2018**, *12*, 1296-1305, DOI: 10.1021/acsnano.7b07529.
- (44) Mukesh, C.; Upadhyay, K. K.; Devkar, R. V.; Chudasama, N. A.; Raol, G. G.; Prasad, K. Preparation of a Noncytotoxic Hemocompatible Ion Gel by Self-Polymerization of HEMA in a Green Deep Eutectic Solvent. *Macromol. Chem. Phys.* **2016**, *217*, 1899-1906, DOI: 10.1002/macp.201600122.
- (45) Pei, X.; Zhao, J.; Ye, Y.; You, Y.; Wei, X. Wormlike micelles and gels reinforced by hydrogen bonding in aqueous cationic gemini surfactant systems. *Soft Matter* **2011**, *7*, 2953-2960, DOI: 10.1039/C0SM01071E.
- (46) Gabriele, F.; Chiarini, M.; Germani, R.; Tiecco, M.; Spreti, N. Effect of water addition on choline chloride/glycol deep eutectic solvents: Characterization of their structural and physicochemical properties. *J. Mol. Liq.* **2019**, *291*, 111301, DOI: 10.1016/j.molliq.2019.111301.
- (47) Terech, P.; Pasquier, D.; Bordas, V.; Rossat, C. Rheological Properties and Structural Correlations in Molecular Organogels. *Langmuir* **2000**, *16*, 4485-4494, DOI: 10.1021/la991545d.
- (48) Rizzo, C.; D'Anna, F.; Marullo, S.; Vitale, P.; Noto, R. Two-Component Hydrogels Formed by Cyclodextrins and Dicationic Imidazolium Salts. *Eur. J. Org. Chem.* **2014**, *2014*, 1013-1024, DOI: 10.1002/ejoc.201301428.

- (49) D'Anna, F.; Vitale, P.; Ferrante, F.; Marullo, S.; Noto, R. The Gelling Ability of Some Diimidazolium Salts: Effect of Isomeric Substitution of the Cation and Anion. *ChemPlusChem* **2013**, *78*, 331-342, DOI: 10.1002/cplu.201300016.
- (50) D'Anna, F.; Vitale, P.; Marullo, S.; Noto, R. Geminal Imidazolium Salts: A New Class of Gelators. *Langmuir* **2012**, *28*, 10849-10859, DOI: 10.1021/la301319u.
- (51) Rizzo, C.; D'Anna, F.; Noto, R.; Zhang, M.; Weiss, R. G. Insights into the Formation and Structures of Molecular Gels by Diimidazolium Salt Gelators in Ionic Liquids or "Normal" Solvents. *Chem. Eur. J.* **2016**, *22*, 11269-11282, DOI: 10.1002/chem.201600670.
- (52) D'Anna, F.; Rizzo, C.; Vitale, P.; Lazzara, G.; Noto, R. Dicationic organic salts: gelators for ionic liquids. *Soft Matter* **2014**, *10*, 9281-9292, DOI: 10.1039/C4SM01360C.
- (53) Marullo, S.; Meli, A.; Giannici, F.; D'Anna, F. Supramolecular Eutecto Gels: Fully Natural Soft Materials. *ACS Sustainable Chem. Eng.* **2018**, *6*, 12598-12602, DOI: 10.1021/acssuschemeng.8b04278.
- (54) Dawn, A.; Kumari, H. Low Molecular Weight Supramolecular Gels Under Shear: Rheology as the Tool for Elucidating Structure–Function Correlation. *Chem. Eur. J.* **2018**, *24*, 762-776, DOI: 10.1002/chem.201703374.
- (55) Saavedra, B.; Meli, A.; Rizzo, C.; Ramón, D. J.; D'Anna, F. Natural eutectogels: sustainable catalytic systems for C–C bond formation reactions. *Green Chem.* **2021**, *23*, 6555-6565, DOI: 10.1039/D1GC01647D.
- (56) Prat, D.; Pardigon, O.; Flemming, H.-W.; Letestu, S.; Ducandas, V.; Isnard, P.; Guntrum, E.; Senac, T.; Ruisseau, S.; Cruciani, P.; Hosek, P. Sanofi's Solvent Selection Guide: A Step Toward More Sustainable Processes. *Org. Process Res. Dev.* **2013**, *17*, 1517-1525, DOI: 10.1021/op4002565.
- (57) Langmuir, I. THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. II. LIQUIDS.1. *J. Am. Chem. Soc.* **1917**, *39*, 1848-1906, DOI: 10.1021/ja02254a006.
- (58) Liu, Y.; Liu, F.; Wang, R.; Yang, X. The Removal of Benzothiophene from Model Diesel on NaY and NiY Zeolites: Equilibrium and Kinetic Studies. *Int. J. Chem. React. Eng.* **2018**, *16*, DOI: doi:10.1515/ijcre-2017-0161.
- (59) Freundlich, H. Über die Adsorption in Lösungen. *Zeit. Phys. Chem.* **1907**, *57U*, 385-470, DOI: 10.1515/zpch-1907-5723.
- (60) Mondal, S.; Dastidar, P. Mixed Ligand Coordination Polymers for Metallogelation and Iodine Adsorption. *Cryst. Growth Des.* **2019**, *19*, 470-478, DOI: 10.1021/acs.cgd.8b01547.
- (61) Zheng, K.; He, C.; Nour, H. F.; Zhang, Z.; Yuan, T.; Traboulsi, H.; Mazher, J.; Trabolsi, A.; Fang, L.; Olson, M. A. Augmented polyhydrazone formation in water by template-assisted polymerization using dual-purpose supramolecular templates. *Polym. Chem.* **2020**, *11*, 1806-1819, DOI: 10.1039/C9PY01476D.
- (62) Li, B.; Wang, B.; Huang, X.; Dai, L.; Cui, L.; Li, J.; Jia, X.; Li, C. Terphen[n]arenes and Quaterphen[n]arenes (n=3–6): One-Pot Synthesis, Self-Assembly into Supramolecular Gels, and Iodine Capture. *Angew. Chem., Int. Ed.* **2019**, *58*, 3885-3889, DOI: 10.1002/anie.201813972.
- (63) Gambhir, D.; Venkateswarulu, M.; Verma, T.; Koner, R. R. High Adsorption Capacity of an sp²/sp³-N-Rich Polymeric Network: From Molecular Iodine Capture to Catalysis. *ACS Appl. Polym. Mater.* **2020**, *2*, 152-158, DOI: 10.1021/acsapm.9b00926.
- (64) Liao, P.; Feng, X.; Fang, H.; Yang, Z.; Zhang, J. Stabilized nanotube and nanofiber gel materials toward multifunctional adsorption. *Colloids Surf., A* **2021**, *628*, 127347, DOI: 10.1016/j.colsurfa.2021.127347.