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Enhancing hexachlorocyclohexane solubility with surfactants and ionic liquids

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ABSTRACT

Surfactant-enhanced remediation of soil can increase the solubility of hydrophobic organic contaminants in water and improve their removal. In this study, the effect of 24 traditional surfactants and surface-active ionic liquids (SAILs) on the solubility of hexachlorocyclohexane isomers (α-, β-, γ-, δ-HCH) was evaluated in batch-type experiments. The combination of two different proportions of a cationic SAIL and an anionic surfactant was also assessed. The solubilisation capacity of the surfactant varied depending on its concentration and structure, but also the HCH isomer considered. In general, the anionic surfactants yielded the best results, increasing solubilisation of HCH up to 2.4 times compared to the control (pure water). α-HCH and γ-HCH isomers were more easily solubilised than β-HCH and δ-HCH regardless of the surfactant's type. The main advantage of ionic liquids being their tunability, some clues are given for formulating surfactants to enhance the solubilisation of HCH. The combination of a traditional surfactant and a SAIL influenced the critical micelle concentration, but not the solubilisation of the contaminant. Further studies on the use of blends for this application are required. The increase of solubility achieved with the studied surfactants encourages their application in washing HCH-contaminated soils through solubility enhancement.

1. Introduction

Hexachlorocyclohexanes (HCHs) are a group of synthetic organochlorine compounds that were used as broad-spectrum pesticides worldwide during the mid-20th century. Originally, they were commercialised as a mixture of isomers, but due to the exclusive insecticidal efficacy of γ-HCH, this later became the only component in such formulations, sold under the name of lindane [1]. However, the process of isolating γ-HCH resulted in substantial quantities of residual HCH isomers, primarily α- and β-HCH, which were disposed in the proximities of production facilities lacking adequate control measures.

α-, β-, and γ-HCH isomers were included in the Stockholm Convention persistent organic pollutants (POPs) list in 2009 due to their high persistence and considerable toxicity, leading to their prohibition in most countries [2]. It is well-established that these isomers, along with δ-HCH, present carcinogenic, neurotoxic, immunotoxic, and hepatotoxic risks to both wildlife and human populations [3]. Despite severe regulations and bans, trace amounts of these detrimental isomers persistently contaminate soil, water, animal tissues and food products, showcasing the historical legacy of these POPs [4–7]. This pressing situation demands an immediate and efficient solution for mitigating HCH-induced environmental contamination.

In this context, bioremediation is emerging as a promising and sustainable approach for the decontamination of soils with POPs [8], including HCHs [9]. Microbial degradation, biosorption microbes, and phytoremediation are tested methods to remove lindane from soil [10]. They are low-cost, environmentally-sound, and they can be used in situ. However, the inherently low bioavailability of HCH compounds usually reduces the efficiency of bioremediation processes, decreasing the success of these methods, which are also characterised by requiring long treatment times. Physico-chemical treatments are the suitable alternative. Thermal desorption has been tested both in- and ex-situ [10], but the energy requirements and the need to treat the generated off-gas make them high-cost methods. In situ chemical oxidation uses

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expensive strong chemical oxidizers and can lead to secondary contamination of soil and groundwater. Those problems are also associated to solvent extraction with traditional organic solvents. Nanoremediation may offer a more cost-effective option for lindane contaminated soil, but the strong negative effect of nanoparticles in the environment and human health is a serious drawback in the application of the method. Soil washing (ex-situ) or flushing (in-situ) with aqueous solutions are promising alternatives [11,12]. Currently there is an increasing interest in the use of surfactants for remediation of contaminated soils [13,14], as key components of washing formulations. The concentration of the surface-active agent in the aqueous solution is usually very low. However, its cost and retention in the soil are key factors in the feasibility of the process.

Surfactants are amphipathic molecules, able to form micelles in aqueous solutions [15]. Thus, surfactants can encapsulate hydrophobic contaminants, such as HCH compounds, within these micellar structures. This encapsulation enhances the solubility of the contaminants in water, facilitating their treatment after leaching. Both synthetic surfactants and biosurfactants have demonstrated their capacity to solubilise diverse hydrophobic organic contaminants [16,17].

Within this framework, surface-active ionic liquids (SAILs) are emerging as a promising alternative to traditional surfactants. SAILs are characterised by their low melting point (below 100 °C) and a strong tendency for micellization [18]. In addition, they have a wide liquidus range, low volatility, and a reduced risk of flammability. However, their most attractive attribute is likely their tunability, as anions and cations of SAILs can be easily tuned to prepare task-specific compounds [19].

The ability of surfactants to dissolve contaminants depends on two key factors: the nature of the pollutant itself and the chemical structure of the surface-active agent [20]. It has been proven that different types of these chemicals, such as cationic, anionic, and nonionic surfactants, possess varying abilities to dissolve contaminants [21]. Other authors have also explored how the alkyl chain length and the counterion (in the case of ionic surfactants) can influence the effectiveness of the surfactants used [22–24].

The hydrophilic-lipophilic balance (HLB) of surfactants is a widely used parameter to measure the affinity of the surfactants for oil or water. Surfactants having an HLB value greater than 9 are water soluble and form oil in water emulsions, the HLB required being dependent on the type of oil or contaminant [25]. Unfortunately, the determination of the HLB of SAILs is still an undeveloped topic.

Surfactant adsorption in the soil, biodegradability, toxicity, and cost, are considerations that must be thoroughly assessed when selecting a surface-active compound in surfactant-enhanced soil washing applications. However, the first step is finding a suitable surfactant able to improve the solubilisation in water of the specific contaminant. Nonionic surfactants are usually preferred in singular systems [21]. Mixed systems are being studied for their potential to diminish surfactant adsorption, lower the critical micelle concentration (CMC), and improve solubilisation capacity of the individual compounds [26]. Research in surfactant-enhanced soil remediation has been predominantly focused on Polycyclic Aromatic Hydrocarbons (PAHs) (see e.g. [27]) and Non-Aqueous Phase Liquids (see e.g. [28]). Studies on HCH are relatively scarce and combine different techniques such as washing and biodegradation or electrochemical oxidation [29–32]. Similarly, investigation on the solubilisation of different isomers (not exclusively HCHs) is also very limited [33,34]. For this reason, it is imperative to investigate how the application of surface-active compounds influences the apparent solubility of diverse HCH isomers for remediation applications. The aim of this study is to evaluate the impact of 24 surface-active compounds (comprising traditional surfactants and SAILs) with varying chemical natures (cationic, anionic, and nonionic) on the solubility of HCHs in water. Additionally, the synergistic effect of mixing a cationic SAIL and an anionic surfactant is thoroughly investigated. This paper sheds light on HCHs solubilisation enhancement with surface-active compounds, crucial for applying surfactant-based technologies to soil remediation.

2. Materials and methods

2.1. Materials

HCH isomers (Fig. 1) with a purity of 98.0 wt% for α-HCH, 97.5 wt% for β-HCH, 98.6 wt% for γ-HCH and 98.6 wt% for δ-HCH were obtained from Dr. Ehrenstorfer.

Cationic and anionic traditional surfactants and SAILs used in this work are shown in Table 1. The abbreviated name, source, purity, structure, and CMC of each compound are also presented. Table 2 shows these data for the nonionic surfactants. In the case of these chemicals, the HLB is available and it is also presented in the table.

Some SAILs were synthesised in the laboratory. [C_8C_1im][OAc] was synthesised via metathesis reaction by mixing [C_8C_1im]Cl and potassium acetate in 2-propanol for 48 h under stirring. Precipitated KCl was removed via filtration, and 2-propanol was eliminated using a rotary evaporator. The sample was dissolved several times in cold acetone and filtered until the KCl was completely eliminated. The chloride content was determined employing ionic chromatography. A final value of 0.009 mass fraction of chloride content was obtained. A similar procedure was applied to the synthesis of 2-hydroxyethylammonium-Alfoterra®. In this case, Alfoterra®145-4S 90 and 2-hydroxyethylammonium chloride were mixed to obtain the desired product. The final chloride content was 0.001 mass fraction. Choline dodecanoate was synthesised by dropwise addition of dodecanoic acid (1:1) to an aqueous solution of cholinium bicarbonate while stirring at ambient temperature and pressure. Water was then removed using a rotary evaporator. In all cases, synthesised products were purified under high vacuum to remove residual volatile compounds. In addition, two combinations of C1EG (cationic SAIL) and SDBS (anionic surfactant) were studied: Blend 1 (55.3 wt% C1EG and 44.7 wt% SDBS) and Blend 2 (26.3 wt% C1EG and 73.7 wt% SDBS). These mixtures were selected due to their excellent capacity to solubilise oil and their low adsorption on carbonate rocks [38].

2.2. Methods

The CMC of surfactants that were not previously characterised in the literature was determined according to the Wilhelmy plate method. The surface tension of a series of different solutions of the surfactant at varying concentrations was measured with a Krüss *K*11 tensiometer at

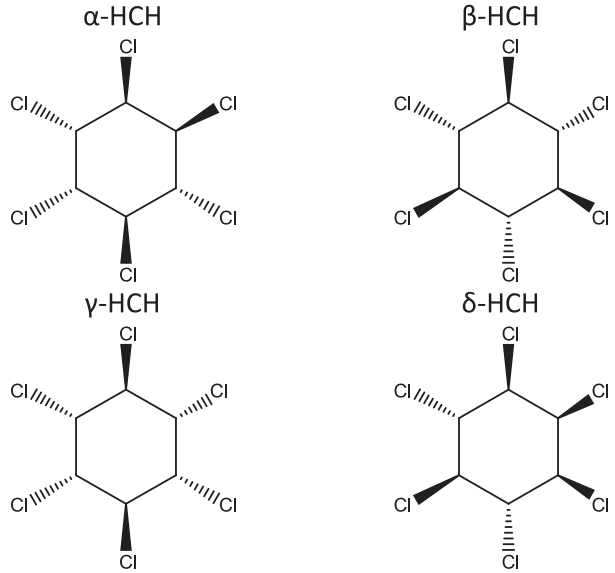
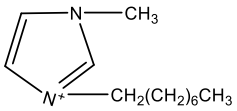
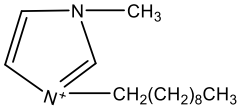
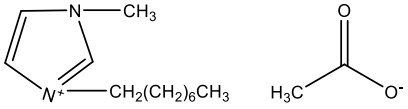
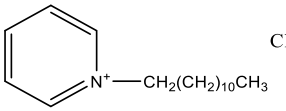
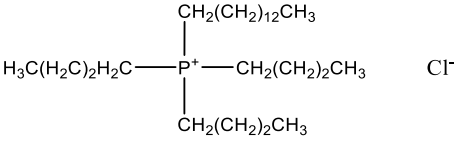
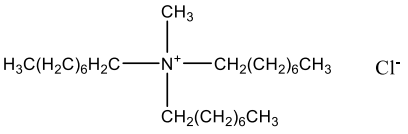
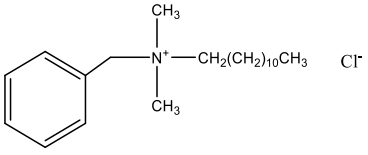
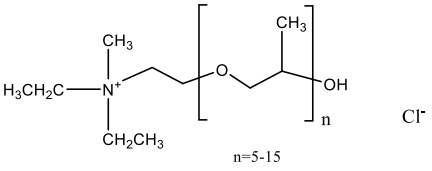
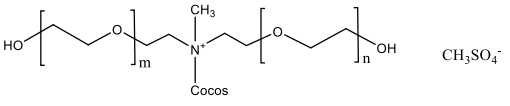
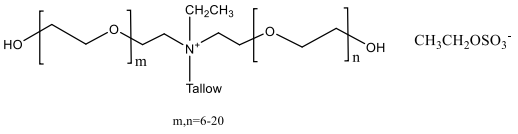
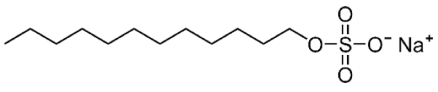
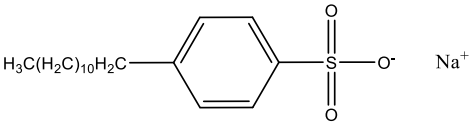


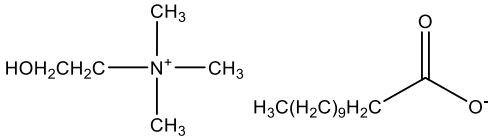
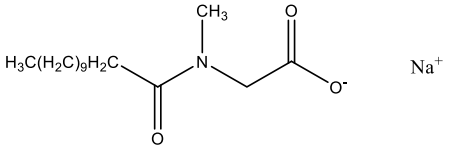
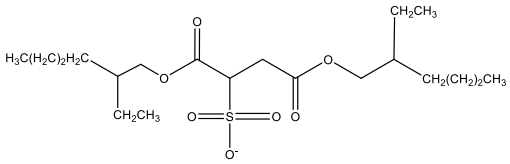
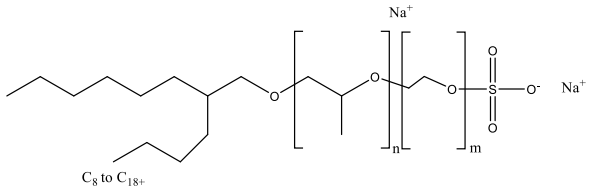
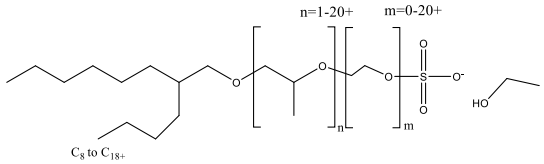
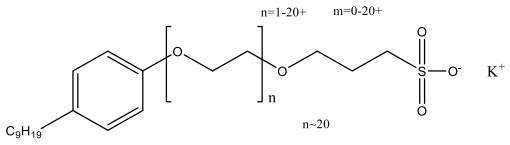
Fig. 1. Chemical structure of HCH isomers.

Table 1
Cationic and anionic traditional surfactants and SAILs used in this study.

Compound	Abbreviation	Source	Purity (wt%)	Structure	CMC (mg/L)
Cationic surface-active compounds					
1-Octyl-3-methylimidazolium chloride	$[C_8C_1im]Cl$	Sigma-Aldrich	>97		438.48 [35]
1-Decyl-3-methylimidazolium chloride	$[C_{10}C_1im]Cl$	Sigma-Aldrich	96		14805.08 [36]
1-Octyl-3-methylimidazolium acetate	$[C_8C_1im][OAc]$	Synthesised	99		11153[1]
1-Dodecylpyridinium chloride	$[C_{12}py]Cl$	Merck	>93		4334.85 [37]
Tributyltetradecylphosphonium chloride	$[P_{4\ 4\ 4\ 14}]Cl$	Solvay	>90		435 [38]
Methyltrioctylammonium chloride	$[N_{1\ 8\ 8\ 8}]Cl$	Sigma-Aldrich	>93		808.32 [39]
Benzyldimethyldodecylammonium chloride	$[N_{1\ 1\ 12\ Bz}]Cl$	Sigma-Aldrich	>99		2991.91 [40]
Poly[oxy(methyl-1,2-ethandiyl)] alpha-[2-(diethylmethylammonium) ethyl]- omega-hydroxy chloride	221PG	Iolitec	>95		31170[1]
Cocosalkylpentaethoximethylammonium methylsulfate	C1EG	Iolitec	>95		88.12 [41]
Ethylbis(hydroxyethyl)tallow alkylethoxylated ethylsulfate	T2EG	Iolitec	>95		36.32 [42]
Anionic surface-active compounds					
Sodium dodecylsulphate	SDS	Sigma-Aldrich	>99		2306.96 [43]
Sodium dodecylbenzenesulphonate	SDBS	Sigma-Aldrich	>99		453.02 [44]

(*continued on next page*)

Table 1 (*continued*)

Compound	Abbreviation	Source	Purity (wt%)	Structure	CMC (mg/L)
Choline dodecanoate	[Ch][ODo]	Synthesised	99		7432.64 [45]
Sodium N-lauroylsarcosinate	Sarkosyl	Sigma-Aldrich	>99		3725.93 [46]
Sodium dioctylsulfoccinate	AOT	Sigma-Aldrich	>97		1182.53 [47]
Alfoterra®145-4S 90	Na-Alfoterra	Sasol	NA		25.22[1]
2-hydroxyethylammonium-Alfoterra®	$N_{0\ 0\ 0\ 2OH}$-Alfoterra	Synthesised	NA		12.15[1]
Poly(ethylene glycol) 4-nonphenyl 3-sulfopropyl ether potassium salt	Ralufon	Sigma-Aldrich	NA		207.65[1]

NA: Not available.
[1] Obtained from surface-tension measurements (Supplementary information; Table S-1).

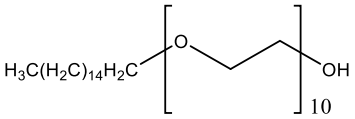
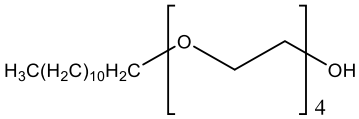
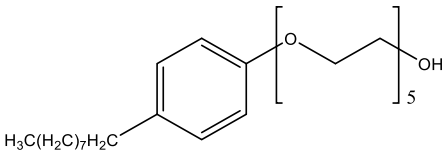
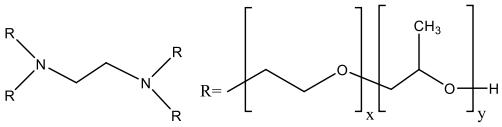
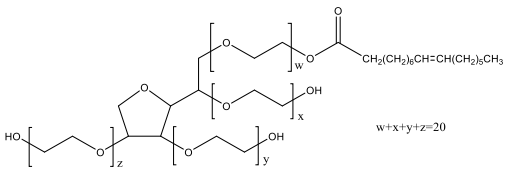
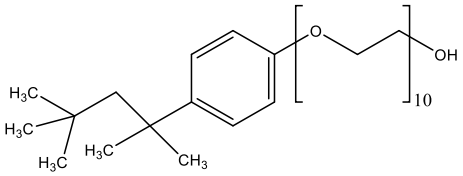
298.15 K. The CMC results from the intersection between the regression straight line of the linearly dependent region and the straight line passing through the plateau (see Table S1 and Figure S1 of the Supplementary Information).

The solubilisation capacity of HCH isomers was determined for each surface-active compound. To that aim, stock solutions of the traditional surfactants or SAILs were prepared in pure water at concentrations of 5 g/L and 15 g/L. Additionally, in the case of nonionic surfactants and due to their low CMCs, a concentration of 15 mg/L was also tested. Stock solutions of all the HCH isomers were prepared with a concentration of 5 g/L in acetone. The required quantities of surfactant and HCH solutions were mixed to obtain a final concentration of 50 mg/L for α-, γ-, and δ-HCH and 2 mg/L for β-HCH in surfactant solutions. These concentrations were approximately ten times higher than reported solubility limit in water [51]. In addition, a control solution (without surfactant) was also prepared. The weighing was carried out on a Mettler AE-100 analytical balance.

All test and control solutions were agitated for 24 h at room temperature until equilibrium was attained. Subsequently, the aqueous phase was separated via centrifugation (HettichTM Zentrifugen EBA 21; 3000 rpm, g Force = 704, 10 min). The dissolved HCH was then extracted using hexane (1:1, v/v) in an ultrasound bath (Ultrasons, J. P. Selecta, S. A.) for 20 min. It is noteworthy that this extraction method yielded recovery rates higher than 95 % for all isomers (data not shown). Following extraction, the organic phase was separated, and any remaining water was removed using anhydrous Na_2SO_4. The resulting extracts were subsequently stored at −4°C until analysis. Pyrex® screw cap test tubes with PTFE lined caps were used throughout the experiments to prevent the adsorption of HCH isomers to the laboratory material. All the tests were carried out in triplicate.

HCH extracts were quantified by gas chromatography-mass spectrometry (Model 450 GC-Model 220 MS Agilent Technologies). Chromatographic separation was carried out on a Trace Gold 5SILMS column (30 m x 0.25 mm x 0.25 μm; Thermo Scientific) under the following operational conditions: temperature 80 °C (1.5 min), increased in 30 °C/min to 180 °C (maintained for 1 min). Subsequently, temperature was increased by 3 °C/min to 200 °C and then 40 °C/min to 290 °C (maintained for 0.25 min). Helium was used as the carrier gas at a constant flow rate of 1 mL/min. The injector temperature was 280 °C. To carry out the experiment, 1 μL of sample was injected in split/splitless mode, and the mass spectrometer was operated in tandem mode. The molecules were ionized by electron impact, and the temperature of the ion trap was adjusted to 220 °C. Calibration standards with a concentration ranging from 1 to 5000 μg/L were prepared from 5 g/L stock solutions, in accordance with the concentration of each HCH isomer. Internal standards, maintained at a constant concentration of 250 μg/L, consisted

Table 2
Nonionic surfactants employed in this study.

Compound	Abbreviation	Source	Purity (wt%)	Structure	CMC (mg/L)	HLB[2]
Polyoxyethylene (10) cetyl ether	Brij C10	Sigma-Aldrich	>97		1.37 [48]	12
Polyethylene dodecyl ether	Brij L4	Sigma-Aldrich	>99		0.333 [49]	9
Polyoxyethylene (5) nonylphenlyether	Igepal CO-520	Sigma-Aldrich	NA		208.55 [50]	10
Ethylenediamine tetrakis (ethocylate-block-propxylate)tetrol	Tetronic 90R4	Sigma-Aldrich	>99.9		28.96[1]	1–7
Polyoxyethylenesorbitan monooleate	Tween 80	Sigma-Aldrich	NA		22 [43]	15
Polyethyleneglyco *tert*-octylphenylether	Triton X-100	Sigma-Aldrich	NA		187.85 [43]	13.5

NA: Not available.
[1] Obtained from surface-tension measurements (Supplementary Information, Table S1).
[2] Obtained from manufacturer.

of a mixture of deuterated compounds, including 1,4-dichlorobenzene-d4, acenaphthene-d10, chrysene-d12, naphthalene-d8, perylene-d12, and phenanthrene-d10 (Internal Standards Mix 33, Dr. Ehrenstorfer). Phenanthrene-d10 was selected as the internal standard due to its similarity in retention time to that of the HCH isomers.

Finally, statistical analysis of the results was carried out. Unifactorial ANOVA and a post hoc Bonferroni test ($p < 0.05$) were used to determine any differences in the solubility of the HCH relative to the control, for each HCH isomer and for the sum of all isomers (ΣHCH). The analyses were conducted using IBM SPSS Statistics 25.0 software.

3. Results

The effect of surface-active compounds at the different studied concentrations in the solubility of ΣHCH (total HCH, considering all the isomers) was assessed. Moreover, the effect on the individual isomers was also analysed. All the results presented in this section were normalised relative to the control. Thus, a value of 1 indicates a solubility equal to that in water and values greater than 1 indicate an increase in solubility. Results are expressed as mean values ± standard error ($n = 3$). The experimental solubilities of the HCH isomers in the control system followed the previously reported order of magnitude: $\delta > \gamma > \alpha > \beta$, and the values obtained are within the range of values determined by other authors (mean values of 10.87 > 6.09 > 2.68 > 0.86 mg/L, respectively) [51,52].

3.1. Cationic surface-active compounds

The effect of cationic SAILs (all the compounds show melting or glass transition temperatures below 100 °C) in the solubility of ΣHCH is presented in Fig. 2. The degree of solubilisation varied depending on the structure and concentration of the surface-active compound used. According to Fig. 2, most compounds increased the solubility of ΣHCH in comparison to the control. However, in the case of $[N_{1\ 8\ 8\ 8}]Cl$ and $[C_8C_1im]Cl$ (both tested surfactant concentrations were higher than CMC), the presence of the surfactant had a negative effect on the solubilisation of the contaminant. Similarly, $[C_8C_1im][OAc]$ also showed a negative effect, even using a surfactant concentration of 15 g/L (higher than its CMC). The effect of 221PG was negligible but this was expected due to the high CMC of this compound (see Table 1). In the case of $[C_{10}C_1im]Cl$, only the highest concentration of surfactant (with a value slightly higher than CMC) led to a positive effect.

Regarding the surface-active compounds with positive effect, in general higher concentrations were more effective (the only exception being the case of $[P_{4\ 4\ 4\ 14}]Cl$). The HCH solubilisation capacity of C1EG and T2EG increased by 30–45 % when increasing the concentration from 5 to 15 g/L. This effect is much more pronounced in the case of $[N_{1\ 1\ 12\ Bz}]Cl$. A concentration of 5 g/L of this surfactant resulted in a minimal increase regarding to water solubilisation. However, a higher concentration of 15 g/L, resulted in a solubility two times higher compared to the control.

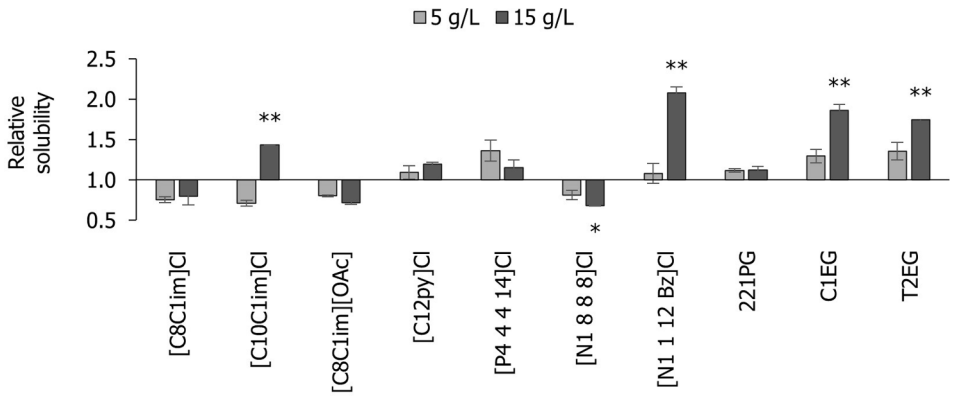


Fig. 2. Effect of cationic surface-active compounds on the water solubility of ΣHCH. Asterisks indicate significant differences relative to the control (*$p < 0.05$ and **$p < 0.01$).

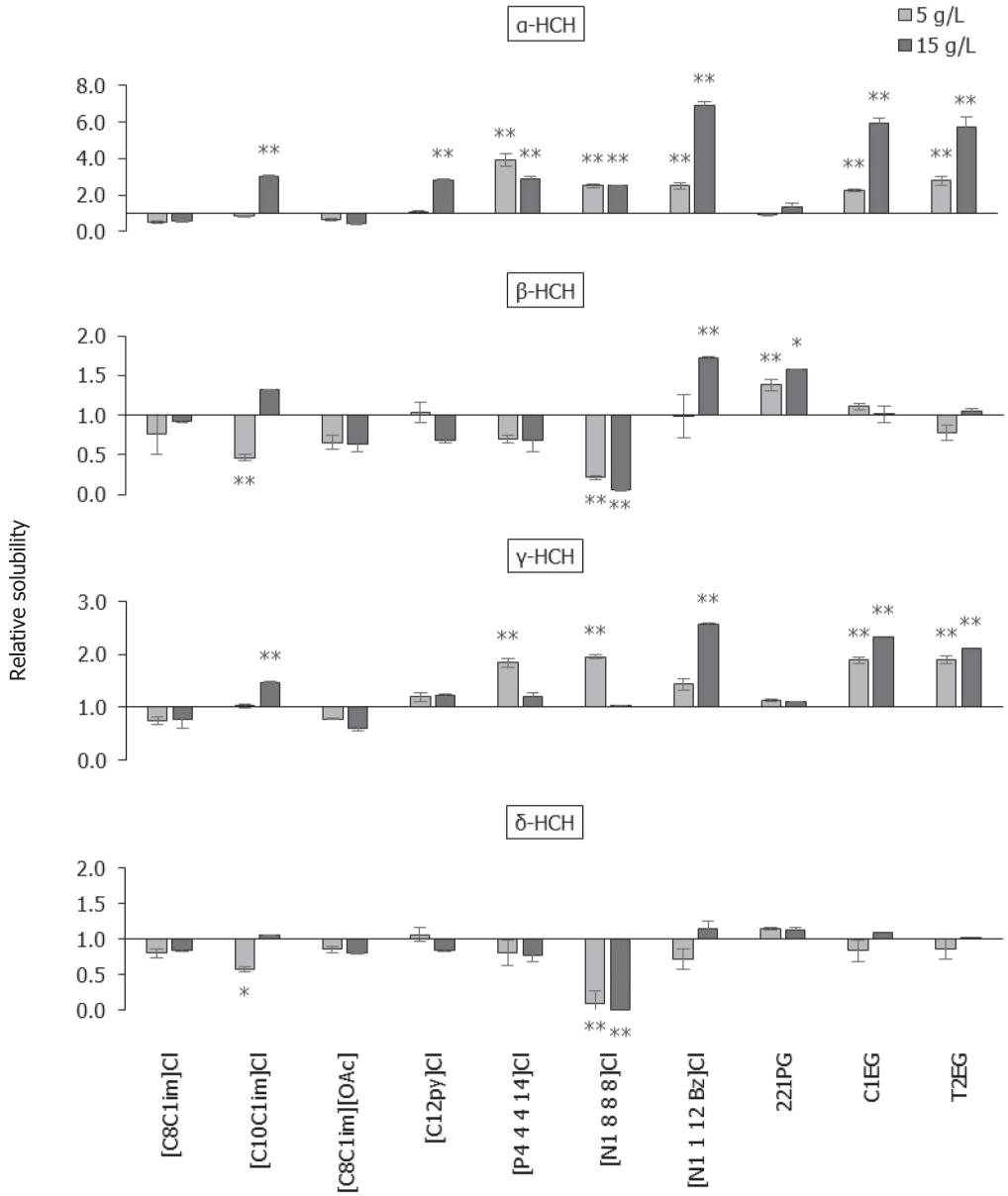


Fig. 3. Changes in the aqueous solubility of α-, β-, γ- and δ-HCH isomers in the presence of cationic surfactants at 5 and 15 g/L. Asterisks indicate significant differences relative to the control (*$p < 0.05$ and **$p < 0.01$).

The head group of the surfactants but mainly the hydrophobic tails and the functional groups that they contain are significant parameters in the ΣHCH solubilisation. The effect of alkyl chain length is likely the most important parameter, as it affects the shape and size of the micelles and aggregations formed. Regardless of the type of head group, the utilization of SAILs with shorter alkyl chain lengths such as [$N_{1\ 8\ 8\ 8}$]Cl, [C_8C_1im]Cl, or [C_8C_1im][OAC], negatively affected the aqueous solubility of ΣHCH. In contrast, the use of surface-active compounds with longer alkyl chains improved the results. This is easily seen comparing solubilisations achieved with [C_8C_1im]Cl and [$C_{10}C_1$im]Cl. Results achieved with this last SAIL improved those found with [C_{12}py]Cl or [$P_{4\ 4\ 4\ 14}$]Cl, with a longer alkyl chain length, so in principle, an imidazolium ring would be preferred. However, the best results were achieved with ammonium SAILs such as T2EG and C1EG (relative solubilities of 1.8 and 1.9, at 15 g/L, respectively), both a mixture of tail-branched surfactants of different lengths, and mainly with [$N_{1\ 1\ 12\ Bz}$]Cl (relative solubility was 2 at 15 g/L). The presence of an aromatic ring attached to the head group seems to positively influence the solubilisation capacity of the ammonium surfactant. Lastly, no differences were observed when altering the nature of the counterion, as evidenced by the comparison between [C_8C_1im]Cl and [C_8C_1im][OAc].

The effect of cationic surface-active compounds on the solubility of the different HCH isomers is presented in Fig. 3. In general, the α-HCH and to a lesser extent γ-HCH isomers were the most readily solubilised, reaching maximum solubility values in the presence of [$N_{1\ 1\ 12\ Bz}$]Cl (α-HCH: ca. 6 times the control and γ-HCH: ca. 3 times the control). β-HCH was, in general, less soluble than the α and γ isomers. It was only solubilised in presence of [$N_{1\ 1\ 12\ Bz}$]Cl, 221PG, and [$C_{10}C_1$im]Cl. Surfactants leading to good results in the solubilisation of ΣHCH such as T2EG and C1EG, however, had a negative or negligible effect on this specific isomer. Worse results were found with δ-HCH: decrease or slight increase in solubilities were found with all the surfactants.

3.2. Anionic surface-active compounds

The effect of anionic surfactants (SDS, SDBS, and AOT) and SAILs ([Ch][Odo], Sarkosyl, Alfoterra, $N_{0\ 0\ 0\ 2OH}$-Alfoterra, and Ralufon) on the solubility of ΣHCH is presented in Fig. 4. As in the case of cationic surfactants, the degree of solubilisation varied depending on the structure and concentration of the surface-active compound used, being favoured by the highest concentration (in the case of Ralufon and Na-Alfoterra, a negligible effect of concentration was observed). The solubility of ΣHCH was increased by the presence of all the tested anionic surfactants except for [Ch][ODo] at a concentration of 5 g/L, which is below its CMC.

SDBS, AOT, [Ch][Odo], and Sarkosyl were the anionic surfactants that, at a concentration of 15 g/L most increased the solubility of ΣHCH, showing relative solubilities of 2.4, 2, 2.4 and 2.2, respectively. Not only the length of the hydrocarbon groups, but also the presence of functional groups as –COO- or aromatic rings, seems to play an important role in the performance of the surfactants. For instance, performance of SDBS is clearly better than SDS. Both have the same alkyl chain length, but the latter has a phenyl ring attached to the hydrophilic group. Na-Alfoterra and $N_{0\ 0\ 0\ 2OH}$-Alfoterra led to similar results, so the counterion did not appear to affect the solubilisation potential of the compounds.

The effect of anionic surface-active compounds on the solubility of the different HCH isomers is presented in Fig. 5. In general, and as in the case of cationic surfactants, the solubility of α- and γ-HCH showed the most significant improvement. The efficacy of SDBS, AOT, [Ch][Odo], and Sarkosyl solubilising ΣHCH particularly applies to δ-HCH, increasing its solubility with respect to water from 1.4 to 1.6 times (15 g/L of surfactant). The only surfactants able to significantly increase the β-HCH solubility were AOT and SDBS with relative solubilities of 2 and 4.6, respectively, at 15 g/L.

3.3. Nonionic surfactants

The effect of nonionic surface-active compounds on the solubility of ΣHCH is presented in Fig. 6. In this case, and due to the low CMC of this kind of surfactants, besides 5 and 15 g/L, a concentration of 15 mg/L was also tested. Even though this concentration is higher than the CMC of Brij C10, Brij L4, and Triton X-100, no enhancement of ΣHCH solubility in water was observed at this low surfactant concentration. Fig. 6 shows that the intermediate concentration (5 g/L) led to the highest relative solubilities in all the cases except for Tetronic 90R4.

Brij C10 and Triton X-100 yielded the best results, increasing ΣHCH solubility in 1.7 and 2.1 times, respectively, compared to the control solution. Thus, an intermediate HLB seems to be favourable for solubilisation enhancement. The HLB values are 12 for Brij C10 and 13.5 for Triton X-100 (Table 2). Brij C10 and Brij L4 are both nonionic ethoxylated alcohols, and again the longest hydrophobic tail of the former led to better results. The highest number of ethylene-oxide units of Triton X-100 in comparison to Igepal CO-520, increases its hydrophilicity (consequently its HLB) and seems to be the reason for its better performance.

The effect of nonionic surface-active compounds on the solubility of the different HCH isomers is presented in Fig. 7. As in the case of the previously studied surfactants, α- and γ-HCH were the most efficiently solubilised isomers. With an intermediate concentration of surfactant (5 g/L) all the surfactants, except Tetronic 90R4, showed positive relative solubilities. It is worth mentioning that this surfactant at the highest concentration (15 g/L) was able to improve the performance of water solubilisation with all the isomers but α-HCH. The good performance of Triton X-100, at 5 g/L, regarding ΣHCH is not only due to its capacity for solubilising α- and γ-HCH isomers (with relative solubilities of 5 and 2.2, respectively) but also β- and δ-HCH (with relative solubilities of 2.2 and

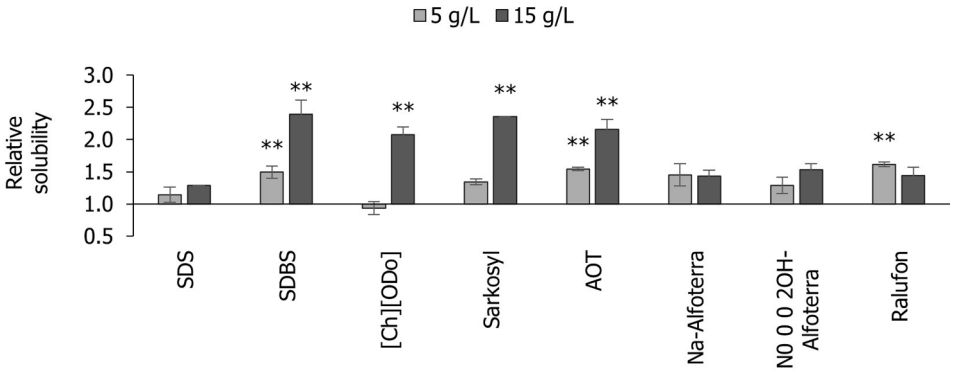


Fig. 4. Effect of anionic surface-active compounds on the water solubility of ΣHCH. Asterisks indicate significant differences relative to the control (*$p < 0.05$ and **$p < 0.01$).

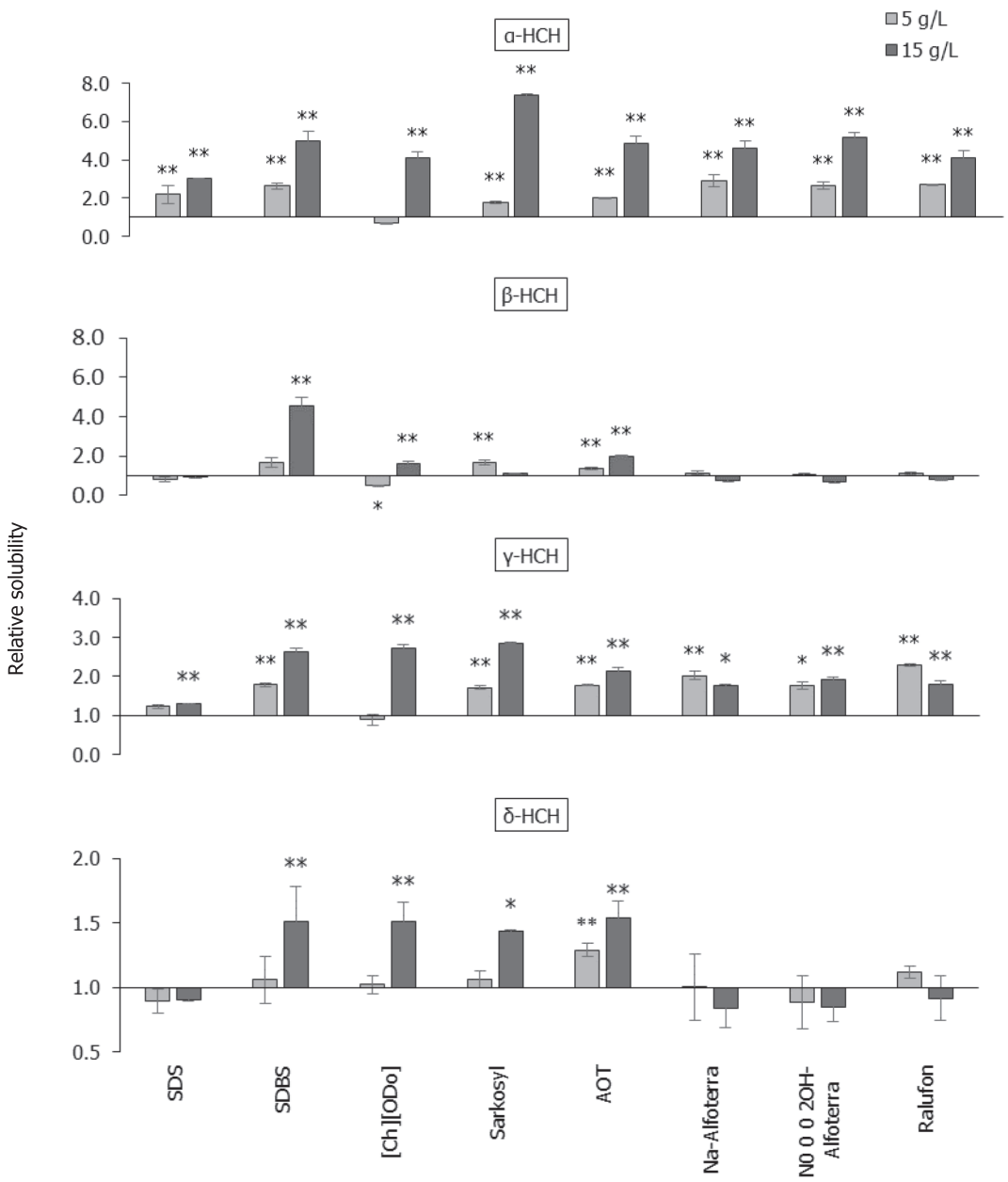


Fig. 5. Changes in the aqueous solubility of α-, β-, γ- and δ-HCH isomers in the presence of anionic surfactants at 5 and 15 g/L. Asterisks indicate significant differences relative to the control (*p < 0.05 and **p < 0.01).

1.4, respectively). Nonetheless, for the recalcitrant isomers, Brij C10 only showed a significative positive performance with β-HCH, showing a relative solubility of 1.7.

3.4. Synergistic effects of a cationic SAIL and an anionic surfactant

Two blends of the SAIL C1EG and the traditional surfactant SDBS were selected to enhance HCH solubilisation. The selected concentrations were 55.3 and 26.3 wt% C1EG. It has been shown in a previous work [41] that these two blends, in salt solutions, were able to successfully extract oil in enhanced oil recovery processes. Moreover, the formation of electrostatically neutral complexes (catanionic micelles) was found the reason for a low adsorption in rocks, this being a promising factor also for application in soil washing.

The solubilisation capacity of blends 1 (55.3 wt% C1EG) and 2 (26.3 wt% C1EG) is shown in Table 3. The results show that an increase of the concentration from 5 to 15 g/L did not improve the results of the solubilisation. The ion pairs formed by blending cationic and anionic species exhibit unique properties such as lower CMC than the individual components. CMC of blend 1 and 2 are 10.5 mg/L and 16.9 mg/L, respectively [41]. The lowest surfactant concentration tested clearly exceeded these values.

At 5 g/L, Blend 2 exhibited superior solubilisation of ΣHCH compared to Blend 1, with the relative solubility achieved (1.5) similar to that obtained with SDBS (1.5) and greater than that obtained with C1EG (1.3). Blend 1 only enhanced the results of Blend 2 in the case of α-HCH, yielding a relative solubility of 5.3, which also markedly surpassed the results achieved with the individual components at the same concentration (2.6 with SDBS and 2.3 with C1EG). Blend 2 performed better for the rest of the isomers, but it only slightly improved the results achieved with the pure surfactants for γ-HCH, and it worsened those of the most recalcitrant isomers (β- and δ-HCH). Nevertheless, overall,

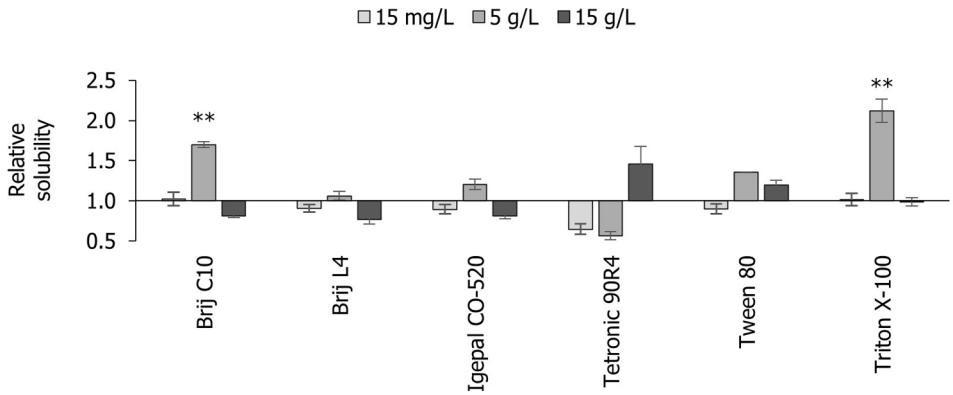


Fig. 6. Effect of nonionic surface-active compounds on the water solubility of ΣHCH. Asterisks indicate significant differences relative to the control (*$p < 0.05$ and **$p < 0.01$).

using the highest concentration (15 g/L) of either SDBS or C1EG generally resulted in higher relative solubilities than those achieved with the blends.

4. Discussion

The solubilisation efficacy of the investigated surface-active compounds depended on their concentration and structure, as well as the specific HCH isomer (α-, β-, γ- or δ-HCH). Surfactant concentration was fixed in order to identify the highest solubilisation at a given concentration of chemical. Below the CMC, as expected, the solubility of HCH isomers was not enhanced. At concentrations higher than CMC, micelles aggregate. At low concentrations, limited or discrete self-assemblies are expected (spherical, prolate, or cylindrical). However, at higher concentrations of surfactant, the assemblies become more ordered, and liquid crystal phases are formed in some cases. Structural parameters such as head group, chain length, counterion, and surfactant concentration affect the size and shape of micellar systems, and therefore the micellar solubilisation capacity. This last is also affected by the hydrophobicity of the solubilised compound [53]. HCH isomers show different hydrophobicity [54], leading to a different solubilisation using the same surfactant and concentration.

Interestingly, the solubility of HCH did not increase consistently with surfactant concentration. In the case of 221PG, tested concentrations were lower than its CMC, which is why the solubilisation achieved with this compound was negligible. This, in general, discounts this surfactant for the application because a quantity of chemical too high would be required. Ideally, surfactants should operate at low doses in washing solutions to minimise remediation costs, especially considering that the effective CMC in the soil–water system tends to be higher than in aqueous solutions [55]. In the case of [Ch][Odo], the minor concentration tested (5 g/L) was also lower than its CMC, reason why only a significative effect was achieved with 15 g/L. In general, both the cationic and anionic compounds tended to produce higher solubility at the highest concentration (15 g/L) due to a larger number of micelles and aggregates formed. However, among surfactants leading to positive relative solubilities, in the case of the anionic Na-Alfoterra and Ralufon, and in the case of the cationic $[P_{4\,4\,4\,14}]Cl$ and 221PG, no positive effect was observed by increasing the concentration. In the case of nonionic surfactants, a concentration of 5 g/L led to the best results (except in the case of Tetronic 90R4). These results may be attributed to the lower CMC of nonionic compounds. In fact, the same behaviour was found with the blends of SDBS and C1EG that exhibit very low CMCs. Micelles of surfactant compounds are continually forming in equilibrium with free monomers. Exceeding a certain concentration may disrupt this equilibrium, destabilizing the forming micelles [20]. Surfactant compounds exhibit their optimal solubilisation capacity within a specific concentration range, consistently higher than the CMC, and with a well-defined upper limit.

Previous reports have shown that nonionic surfactants displayed a greater capacity than cationic and anionic ones to solubilise PAHs [56]. Masrat *et al.* [57] compared the capacity of nonionic, anionic and cationic surfactants to solubilise naphthalene and pyrene, observing that the nonionic compounds produced the best results, as also reported by Sales *et al.* [26]. In this work, in general anionic surfactants performed better for the solubilisation of HCH, a polyhalogenated six-carbon ring. The best relative solubilities achieved for ΣHCH were about 2.4 and they could be achieved with SDBS and Sarkosyl, but close values were also achieved with other anionic (AOT and [Ch][Odo]), cationic $[N_{1\,1\,12\,Bz}]$, and nonionic (Triton X-100) surfactants.

The chemical structure of the surface-active compounds influences the micellar behaviour and, consequently, the solubilisation capacity. In general, the longer the alkyl chain length the greater the HCH solubilisation. This is due to the increase of the size of the hydrophobic nucleus that holds the contaminant. Chun *et al.* [58] showed that the presence of aromatic rings in the alkyl chains of the surfactants favoured the solubilisation of PAHs. That effect was also observed in this study. Additionally, it was also found that the presence of certain functional groups in the hydrocarbon tails (such as –COO- or ethylene-oxide units) could improve solubilisation performance. However, the role of the hydrophilic region in micellization and solubilisation of contaminants remains unclear. Some authors have found that an increase in the length of the polar chain affects the solubilisation capacity of compounds [59], while others have found no such effect [60]. Among cationic surfactants, in this work ammonium ones seem to have performed best. Regarding SAILs, Wang *et al.* [24] noted that the nature of the anion on imidazolium SAILs affected the anion-cation interactions and consequently its CMC and aggregation. In the present study, a significant effect of counterions was not found, even when the surface-active compounds showed different CMC.

In the case of nonionic surfactants at 5 g/L, solubilisation capacity went through a maximum as surfactant HLB increased, with higher relative solubilities at HLB values in the range 12–13.5 (Brij C10 and Triton X-100). Diallo *et al.* [61] found a similar behaviour investigating the solubilisation of aromatic hydrocarbons and chloroethene compounds in micellar solutions of dodecyl alcohol ethoxylates. According to the authors, this is due to two opposing effects: a decrease in solubility with increasing HLB (reduction of hydrophobic nucleus) and the enhancement by electron donor–acceptor complexation.

The synergistic effects of surfactants have been extensively investigated [62] due to their behaviour in soils. Anionic compounds can cause precipitation and cationic surfactants generally show high adsorption. These drawbacks can be surpassed by blending surfactants. Most studies have focused on PAHs, commonly employing a mixture of ionic and nonionic surfactants. While the results in such cases have been very positive, mixtures of ionic-type surfactants are also promising. Mixtures

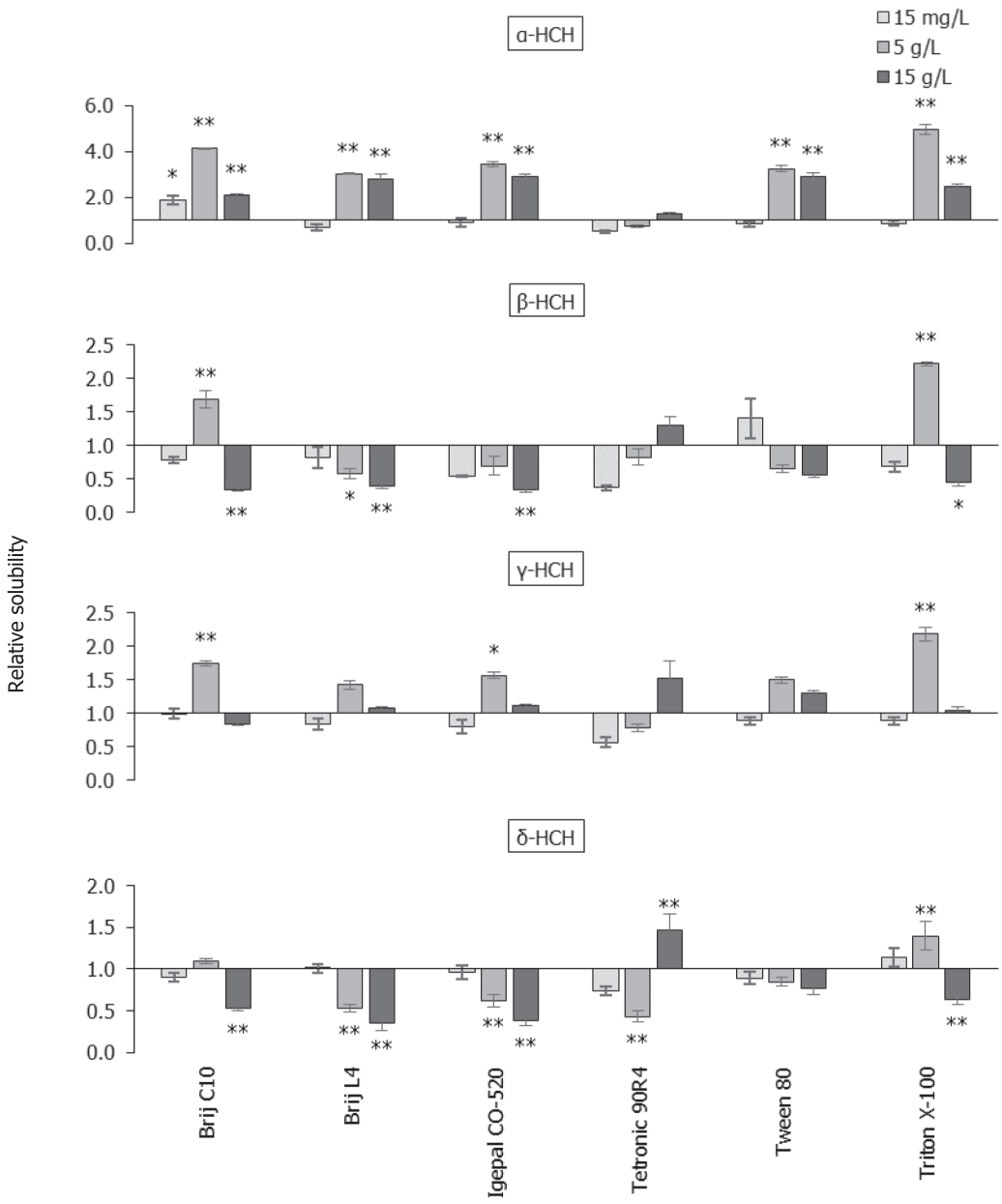


Fig. 7. Changes in the aqueous solubility of α-, β-, γ- and δ-HCH isomers in the presence of nonionic surfactants at 5 and 15 g/L. Asterisks indicate significant differences relative to the control (*p < 0.05 and **p < 0.01).

Table 3
Relative solubilities achieved with blends of C1EG and SDBS. Asterisks indicate significant differences relative to the control (*p < 0.05 and **p < 0.01).

	Blend 1[1]		Blend 2[2]	
	5 g/L	15 g/L	5 g/L	15 g/L
α-HCH	5.30 ± 0.40**	2.74 ± 0.17**	3.76 ± 0.58**	1.92 ± 0.10*
β-HCH	0.63 ± 0.07*	0.41 ± 0.05*	0.83 ± 0.05	0.31 ± 0.03**
γ-HCH	1.95 ± 0.04**	1.12 ± 0.01	2.01 ± 0.11**	0.76 ± 0.03
δ-HCH	0.46 ± 0.16**	0.17 ± 0.07**	0.88 ± 0.13	0.40 ± 0.05**
ΣHCH	1.31 ± 0.06	0.84 ± 0.05	1.45 ± 0.05**	0.71 ± 0.05

[1] Blend 1: 55.3 wt% C1EG + 44.7 wt% SDBS.
[2] Blend 2: 26.3 wt% C1EG + 73.7 wt% SDBS.

of anionic and cationic surfactants display a higher level of synergism [63]. Blends of C1EG and SDBS are promising due to their high surface/interface activity and low adsorption in rocks [41]. However, in this case, the blends tested did not show a significant synergy in the HCH solubilisation when compared with the individual surfactants.

Differences in solubilisation performance were also observed based on the different isomers. As in other studies [29,30], α-HCH and γ-HCH were more easily solubilised than β-HCH and δ-HCH. The α- and γ-HCH isomers, on the one hand, and β- and δ-HCH isomers, on the other, have a similar spatial structure due to the axial (a) or equatorial (e) position of the chlorine atoms: β-HCH, eeeeee and δ-HCH, aeeeee; α-HCH, aaeeee and γ-HCH, aaaeee, potentially explaining the steric effect of chlorines affecting the solubilisation of different isomers. It was observed that solubility of α-HCH increased by 7 times in the presence of $[N_{1\ 1\ 12\ Bz}]Cl$ (15 g/L) or Sarkosyl (15 g/L) and by 5 times in presence of Triton X-100 at a lower concentration (5 g/L). The anionic surfactant SDBS (15 g/L)

resulted the most effective in improving the solubility of β-HCH, increasing its solubility by 5 times. The solubility of γ-HCH was increased by 3 times in the presence of Sarkosyl (15 g/L), SDBS and [Ch][Odo] performing slightly worse at the same concentration. Also anionic surfactants were the most effective to enhance δ-HCH solubility, increasing by 1.5 times in the presence of SDBS, Sarkosyl or [Ch][Odo] (15 g/L) and by 1.4 times in presence of Triton X-100 (5 g/L).

5. Conclusions

Surfactant-enhanced soil washing/flushing is a promising method for the remediation of HCH-contaminated soils, solubility studies being the first required step for the application.

According to their solubilisation capacity, anionic surfactants seem to be the most interesting option for HCH extraction. However, specific cationic and nonionic surface-active compounds also led to significantly higher solubilities than water. The concentration to be used, always higher than CMC, must be optimised in each case. A surfactant with high CMC requires high concentration of the chemical, discouraging its application. In principle, the greater concentration of ionic compounds, the higher the solubilisation. SDBS and Sarkosyl among anionic surfactants and $[N_{1\ 1\ 12\ Bz}]Cl$ and Triton X-100 among cationic and nonionic, respectively, should be considered for future studies. SAILs increase the number of surface-active compounds traditionally used in many applications, such as soil remediation, and allow for the consideration of designing new components. A long hydrophobic tail, the introduction of aromatic rings, considering –COO- units in anionic or ethylene oxide groups in nonionic surfactants are factors to consider in such a design. Also, in the case of this latter type of surfactants, an HLB in the range 12–14 must be considered. The use of blends of surfactants is a research topic to be explored for HCH-contaminated soil remediation.

The tested surfactants all showed a different capacity of solubilisation depending on the HCH isomer. Regardless of the surfactant type, α-HCH and γ-HCH were more easily solubilised than β-HCH and δ-HCH. Cationic surfactants were not able to significantly enhance the δ-HCH solubility.

Soil adsorption, biodegradability and toxicity of surface-active agents leading to the highest solubilities are required future studies to prevent environmental impacts. Surfactants showing high adsorption could potentially become contaminants themselves, underlying the critical importance of considering toxicity and biodegradability, alongside cost, when selecting the most suitable surfactant for the application.

CRediT authorship contribution statement

Zoe Chaos: Writing – original draft, Investigation, Formal analysis, Data curation. **María Balseiro-Romero:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **Beatriz Calviño-Vázquez:** Writing – review & editing. **Alba Somoza:** Writing – review & editing, Visualization, Investigation. **Ana Soto:** Writing – review & editing, Resources. **Carmen Monterroso:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2024.124329.

References

[1] J. Vijgen, The legacy of lindane HCH isomer production. Main report. A global overview of residue management, formulation and disposal, International HCH & Pesticides Association, 2006.
[2] UNEP, 2009. Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009: Text and Annexes. https://wedocs.unep.org/handle/20.500.11822/27568?show=full Last assessed: October, 2023.
[3] S. Adithya, R.S. Jayaraman, A. Krishnan, R. Malolan, K.P. Gopinath, J. Arun, W. Kim, M. Govarthanan, A critical review on the formation, fate and degradation of the persistent organic pollutant hexachlorocyclohexane in water systems and waste streams, Chemosphere 271 (2021) 129866, https://doi.org/10.1016/j.chemosphere.2021.129866.
[4] V. Fuscoletti, L. Achene, F. Gismondi, D. Lamarra, L. Lucentini, S. Spina, E. Veschetti, L. Turrio-Baldassarri, Presence of epsilon HCH together with four other HCH isomers in drinking water, groundwater and soil in a former lindane production site, Bull. Environ. Contam. Toxicol. 95 (2015) 108–115, https://doi.org/10.1007/s00128-015-1516-6.
[5] B. Łozowicka, P. Kaczyński, E. Wolejko, J. Piekutin, A. Sagitov, K. Toleubayev, G. Isenova, E. Abzeitova, Evaluation of organochlorine pesticide residues in soil and plants from East Europe and Central Asia, Desalin. Water Treat. 57 (3) (2016) 1310–1321, https://doi.org/10.1080/19443994.2014.996008.
[6] I. Navarro, A. de la Torre, P. Sanz, M.A. Arjol, J. Fernández, M.A. Martínez, Organochlorine pesticides air monitoring near a historical lindane production site in Spain, Sci. Total Environ. 670 (2019) 1001–1007, https://doi.org/10.1016/j.scitotenv.2019.03.313.
[7] E. Szpyrka, A. Kurdziel, A. Matyaszek, M. Podbielska, J. Rupar, M. Slowik-Borowiec, Evaluation of pesticide residues in fruits and vegetables from the region of South-Eastern Poland, Food Control 48 (2015) 137–142, https://doi.org/10.1016/j.foodcont.2014.05.039.
[8] M. Kumar, S.K. Saggu, P. Pratibha, S.K. Singh, S. Kumar, Exploring the role of microbes for the management of persistent organic pollutants, J. Environ. Manage. 344 (2023) 118492, https://doi.org/10.1016/j.jenvman.2023.118492.
[9] Z. Usmani, M. Kul, T. Lukk, Bioremediation of lindane contaminated soil: exploring the potential of actinobacterial strains, Chemosphere 278 (2021) 130468, https://doi.org/10.1016/j.chemosphere.2021.130468.
[10] European Parliament, Directorate-General for Internal Policies of the Union, Vega, M., Romano, D., Uotila, E., 2016. Lindane (persistant organic pollutant) in the EU. https://data.europa.eu/doi/10.2861/167592. Last accessed: 08-02-2024.
[11] E. Morillo, J. Villaverde, Advanced technologies for the remediation of pesticide-contaminated soils, Sci. Total Environ. 586 (2017) 576–597, https://doi.org/10.1016/j.scitotenv.2017.02.020.
[12] C. Trellu, E. Mousset, Y. Pechaud, D. Huguenot, E.D. van Hullebusch, G. Esposito, M.A. Oturan, Removal of hydrophobic organic pollutants from soil washing/flushing solutions: a critical review, J. Hazard. Mater. 306 (2016) 149–174, https://doi.org/10.1016/j.jhazmat.2015.12.008.
[13] X.H. Mao, R. Jiang, W. Xiao, J.G. Yu, Use of surfactants for the remediation of contaminated soils: a review, J. Hazard. Mater. 285 (2015) 419–435, https://doi.org/10.1016/j.jhazmat.2014.12.009.
[14] S. Bolan, L.P. Padhye, C.N. Mulligan, E.R. Alonso, R. Saint-Fort, T. Jasemizad, C. S. Wang, T. Zhang, J. Rinklebe, H.L. Wang, K.H.M. Siddique, M.B. Kirkham, N. Bolan, Surfactant-enhanced mobilization of persistent organic pollutants: potential for soil and sediment remediation and unintended consequences, J. Hazard. Mater. 443 (2023) 130189, https://doi.org/10.1016/j.jhazmat.2022.130189.
[15] M.J. Rosen, J.T. Kunjappu, Surfactants and interfacial phenomena, 4th ed., John Wiley & Sons Inc, New York, 2012.
[16] P. Das, S. Mukherjee, R. Sen, Improved bioavailability and biodegradation of a model polyaromatic hydrocarbon by a biosurfactant producing bacterium of marine origin, Chemosphere 72 (9) (2008) 1229–1234, https://doi.org/10.1016/j.chemosphere.2008.05.015.
[17] A. Szulc, D. Ambrożewicz, M. Sydow, Ł. Ławniczak, A. Piotrowska-Cyplik, R. Marecik, Ł. Chrzanowski, The influence of bioaugmentation and biosurfactant addition on bioremediation efficiency of diesel-oil contaminated soil: feasibility during field studies, J. Environ. Manage. 132 (2014) 121–128, https://doi.org/10.1016/j.jenvman.2013.11.006.
[18] P. Pillai, A. Kumar, A. Mandal, Mechanistic studies of enhanced oil recovery by imidazolium-based ionic liquids as novel surfactants, J. Ind. Eng. Chem. 63 (2018) 262–274, https://doi.org/10.1016/j.jiec.2018.02.024.
[19] N. Cheng, X. Ma, X. Sheng, T. Wang, R. Wang, J. Jiao, L. Yu, Aggregation behavior of anionic surface active ionic liquids with double hydrocarbon chains in aqueous

solution: experimental and theoretical investigations, Colloids Surf. A Physicochem. Eng. Asp. 453 (2014) 53–61, https://doi.org/10.1016/j.colsurfa.2014.03.083.
[20] A. Patist, S.G. Oh, R. Leung, D.O. Shah, Kinetics of micellization: its significance to technological processes, Colloids Surf. A Physicochem. Eng. Asp. 176 (1) (2001) 3–16, https://doi.org/10.1016/S0927-7757(00)00610-5.
[21] S. Paria, Surfactant-enhanced remediation of organic contaminated soil and water, Adv. Colloid Interface Sci. 138 (1) (2008) 24–58, https://doi.org/10.1016/j.cis.2007.11.001.
[22] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Surfactant-enhanced remediation of contaminated soil: a review, Eng. Geo. 60 (1–4) (2001) 371–380, https://doi.org/10.1016/S0013-7952(00)00117-4.
[23] Benrraou, M., Bales, B.L., Zana, R., 2003. Effect of the Nature of the Counterion on the Properties of Anionic Surfactants. 1. Cmc, Ionization Degree at the Cmc and Aggregation Number of Micelles of Sodium, Cesium, Tetramethylammonium, Tetraethylammonium, Tetrapropylammonium, and Tetrabutylammonium Dodecyl Sulfates. *J. Phys. Chem. B* 107(48): 13432-13440. 10.1021/jp021714u.
[24] H. Wang, J. Wang, S. Zhang, X. Xuan, Structural effects of anions and cations on the aggregation behavior of ionic liquids in aqueous solutions, J. Phys. Chem. B 112 (51) (2008) 16682–16689, https://doi.org/10.1021/jp8069089.
[25] Leermakers, F., Eriksson, J.C., Lyklema, H. 2005. Association Colloids and their Equilibrium Modelling. In: J. Lyklema (Ed.) *Fundamentals of Interface and Colloid Science, Vol. V: Soft Colloids*, Elsevier Academic Press, Amsterdam.
[26] P.S. Sales, R.H. de Rossi, M.A. Fernández, Different behaviours in the solubilisation of polycyclic aromatic hydrocarbons in water induced by mixed surfactant solutions, Chemosphere 84 (11) (2011) 1700–1707, https://doi.org/10.1016/j.chemosphere.2011.04.073.
[27] M. Saeedi, L.Y. Li, J.R. Grace, Simultaneous removal of polycyclic aromatic hydrocarbons and heavy metals from natural soil by combined non-ionic surfactants and EDTA as extracting agents: laboratory columna tests, J. Environ. Manage. 248 (2019) 109258, https://doi.org/10.1016/j.jenvman.2018.03.125.
[28] W. Rongsayamanont, C. Tongcumpou, N. Phasukarratchai, Diesel-contaminated soil washing by mixed nonionic surfactant emulsion and seed germination test, Water Air Soil Pollut. 231 (2020) 267, https://doi.org/10.1007/s11270-020-04649-0.
[29] J.C. Quintero, M.T. Moreira, G. Feijoo, J.M. Lema, Effect of surfactants on the soil desorption of hexachlorocyclohexane (HCH) isomers and their anaerobic biodegradation, J. Chem. Technol. Biotechnol. 80 (9) (2005) 1005–1015, https://doi.org/10.1002/jctb.1277.
[30] N. Manickam, A. Bajaj, H.S. Saini, R. Shanker, Surfactant mediated enhanced biodegradation of hexachlorocyclohexane (HCH) isomers by sphingomonas sp. NM05, Biodegradation 23 (2012) 673–682, https://doi.org/10.1007/s10532-012-9543-z.
[31] G. Zheng, A. Selvam, J.W.C. Wong, Enhanced solubilization and desorption of organochlorine pesticides (OCPs) from soil by oil-swollen micelles formed with a nonionic surfactant, Environ. Sci. Technol. 46 (21) (2012) 12062–12068, https://doi.org/10.1021/es302832z.
[32] M. Muñoz-Morales, M. Braojos, C. Sáez, P. Cañizares, M.A. Rodrigo, Remediation of soils polluted with lindane using surfactant-aided soil washing and electrochemical oxidation, J. Hazard. Mater. 339 (2017) 232–238, https://doi.org/10.1016/j.jhazmat.2017.06.021.
[33] Y. Eda, N. Takisawa, K. Shirahama, Solubilization of isomeric alkanols in ionic micelles, Langmuir 13 (9) (1977) 2432–2435, https://doi.org/10.1021/la960856a.
[34] J. Andreaus, J. Draxler, R. Marr, H. Lohner, The effect of sodium dodecyl sulfate and M-alpha-cyclodextrin on the solubility and partitioning of xylenes in aqueous solutions, J. Colloid. Interface Sci. 185 (2) (1997) 306–312, https://doi.org/10.1006/jcis.1996.4556.
[35] A. Beyaz, W.S. Oh, V.P. Reddy, Ionic liquids as modulators of the critical micelle concentration of sodium dodecyl sulfate, Colloids Surf. B Biointerfaces 35 (2) (2004) 119–124, https://doi.org/10.1016/j.colsurfb.2004.02.014.
[36] J. Łuczak, M. Markiewicz, J. Thöming, J. Hupka, C. Jungnickel, Influence of the Hofmeister anions on self-organization of 1-decyl-3-methylimidazolium chloride in aqueous solutions, J. Colloid Interface Sci. 362 (2) (2011) 415–422, https://doi.org/10.1016/j.jcis.2011.06.058.
[37] L. Tennouga, A. Mansri, K. Medjahed, A. Chetouani, I. Warad, The micelle formation of cationic and anionic surfactants in aqueous medium: determination of CMC and thermodynamic parameters at different temperatures, J. Mater. Environ. Sci. 6 (10) (2015) 2711–2716.
[38] M. Blesic, J.N.C. Lopes, M.C.F. Gomes, L.P.N. Rebelo, Solubility of alkanes, alkanols and their fluorinated counterparts in tetraalkylphosphonium ionic liquids, Phys. Chem. Chem. Phys. 12 (33) (2010) 9685–9692, https://doi.org/10.1039/C003408H.
[39] W. Zhang, S. Jiang, T. Qin, J. Sun, C. Dong, Q. Hu, Effect of ionic liquid surfactants on coal oxidation and structure, J. Anal. Methods Chem. 2019 (2019), https://doi.org/10.1155/2019/1868265.
[40] A. González-Pérez, J. Czapkiewicz, G. Prieto, J.R. Rodríguez, Second critical micelle concentration of dodecyldimethylbenzylammonium chloride in aqueous solution at 25 °C, Colloid Polym. Sci. 281 (2003) 1191–1195, https://doi.org/10.1007/s00396-003-0905-2.
[41] A. Somoza, N. Tafur, A. Arce, A. Soto, Design and performance analysis of a formulation based on SDBS and ionic liquid for EOR in carbonate reservoirs, J. Petr. Sci. Eng. 209 (2022) 109856, https://doi.org/10.1016/j.petrol.2021.109856.
[42] A. Somoza, M.F. García-Mayoral, A. Soto, A formulation based on a cationic surface-active ionic liquid and an anionic surfactant for enhanced oil recovery at a carbonate reservoir, Fuel 346 (2023) 128363, https://doi.org/10.1016/j.fuel.2023.128363.
[43] A.B. Mandal, B.U. Nair, D. Ramaswamy, Determination of the critical micelle concentration of surfactants and the partition coefficient of an electrochemical probe by using cyclic voltammetry, Langmuir 4 (3) (1988) 736–739, https://doi.org/10.1021/la00081a041.
[44] S.K. Hait, P.R. Majhi, A. Blume, S.P. Moulik, A critical assessment of micellization of sodium dodecyl benzene sulfonate (SDBS) and its interaction with poly(vinyl pyrrolidone) and hydrophobically modified polymers, JR 400 and LM 200, J. Phys. Chem. B 107 (15) (2003) 3650–3658, https://doi.org/10.1021/jp027379r.
[45] R. Klein, D. Touraud, W. Kunz, Choline carboxylate surfactants: biocompatible and highly soluble in water, Green Chem. 10 (2008) 433–443, https://doi.org/10.1039/B718466B.
[46] K. Hąc-Wydro, I. Pałasińska, P. Miśkowiec, The comparative studies on the ability of anionic surfactants to bind lead(II) ions, J. Mol. Liq. 219 (2016) 1071–1077, https://doi.org/10.1016/j.molliq.2016.02.067.
[47] D. Das, J. Dey, A.K. Chandra, U. Thapa, K. Ismail, Aggregation behavior of sodium dioctylsulfosuccinate in aqueous ethylene glycol medium. A case of hydrogen bonding between surfactant and solvent and its manifestation in the surface tension isotherm, Langmuir 28 (45) (2012) 15762–15769, https://doi.org/10.1021/la302876z.
[48] J. Vasiljević, B. Simončič, M. Kert, The influence of a surfactant's structure and the mode of its action during reactive wool dyeing, Tekstilec 58 (4) (2015) 301–313.
[49] Y.T. Goo, C.K. Sa, J.Y. Choi, M.S. Kim, C.H. Kim, H.K. Kim, Y.W. Choi, Development of a solid supersaturable micelle of revaprazan for improved dissolution and oral bioavailability using box-behnken design, Int. J. Nanomedicine 16 (2021) 1245–1259, https://doi.org/10.2147/IJN.S298450.
[50] S.K. Ghosh, P.K. Khatua, S.C. Bhattacharya, Aggregation of non ionic surfactant Igepal in aqueous solution: fluorescence and light scattering studies, Int. J. Mol. Sci. 4 (11) (2003) 562–571, https://doi.org/10.3390/i4110562.
[51] B. Rodríguez-Garrido, Movilidad, biodisponibilidad y degradación inducida de isómeros de hexaclorociclohexano (HCH) en suelos contaminados, University of Santiago de Compostela, 2009. Doctoral thesis.
[52] D. Mackay, W.Y. Shiu, K. Ma, S.C. Lee, Physical-chemical properties and environmental fate of organic pollutants, 2nd ed., Taylor & Francis Group, Florida, 2006.
[53] B.C. Stephenson, A. Goldsipe, K.J. Beers, D. Blankschtein, Quantifying the hydrophobic effect. 1. A computer simulation-molecular-thermodynamic model for the self-assembly of hydrophobic and amphiphilic solutes in aqueous solution, J. Phys. Chem. B 111 (5) (2007) 1025–1044, https://doi.org/10.1021/jp065696i.
[54] K.U. Goss, H.P.H. Arp, G. Bronner, C. Niederer, Partition behavior of hexachlorocyclohexane isomers, J. Chem. Eng. Data 53 (3) (2008) 750–754, https://doi.org/10.1021/je700595y.
[55] S. Laha, B. Tansel, A. Ussawarujikulchai, Surfactant–soil interactions during surfactant-amended remediation of contaminated soils by hydrophobic organic compounds: a review, J. Environ. Manage. 90 (1) (2009) 95–100, https://doi.org/10.1016/j.jenvman.2008.08.006.
[56] S. Lamichhane, K.C. Bal Krishna, R. Sarukkalige, Surfactant-enhanced remediation of polycyclic aromatic hydrocarbons: a review, J. Environ. Manage. 199 (2017) 46–61, https://doi.org/10.1016/j.jenvman.2017.05.037.
[57] R. Masrat, M. Maswal, A.A. Dar, Competitive solubilization of naphthalene and pyrene in various micellar systems, J. Hazard. Mater. 244 (2013) 662–670, https://doi.org/10.1016/j.jhazmat.2012.10.057.
[58] C.L. Chun, J.J. Lee, J.W. Park, Solubilization of PAH mixtures by three different anionic surfactants, Environ. Pollut. 118 (3) (2002) 307–313, https://doi.org/10.1016/S0269-7491(01)00304-9.
[59] I. Xiarchos, D. Doulia, Effect of nonionic surfactants on the solubilization of alachlor, J. Hazard. Mater. 136 (3) (2006) 882–888, https://doi.org/10.1016/j.jhazmat.2006.01.027.
[60] F. Tokiwa, Solubilization behavior of sodium dodecylpolyoxyethylene sulfates in relation to their polyoxyethylene chain lengths, J. Phys. Chem. 72 (4) (1968) 1214–1217, https://doi.org/10.1021/j100850a024.
[61] M.S. Diallo, L.M. Abriola, W.J. Weber, Solubilization of nonaqueous phase liquid hydrocarbons in micellar solutions of dodecyl alcohol ethoxylates, Environ. Sci. Technol. 28 (11) (1994) 1829–1837, https://doi.org/10.1021/es00060a012.
[62] W. Ji, C. Abou Khalil, M.P. Jayalakshmamma, L. Zhao, M.C. Boufadel, Behavior of surfactants and surfactant blends in soils during remediation: a review, Environ. Chall. 2 (2021) 100007, https://doi.org/10.1016/j.envc.2020.100007.
[63] G. Kume, M. Gallotti, G. Nunes, Review on anionic/cationic surfactant mixtures, J Surfactants Deterg. 11 (1) (2007) 1–11, https://doi.org/10.1007/s11743-007-1047-1.