Physico-chemical measurements of CL-20 for environmental applications
Comparison with RDX and HMX

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Abstract

   CL-20 is a polycyclic energetic nitramine, which may soon replace the monocyclic nitramines RDX and HMX, because of its superior explosive performance. Therefore, to predict its environmental fate, analytical and physico-chemical data must be made available. An HPLC technique was thus developed to measure CL-20 in soil samples based on the US Environmental Protection Agency method 8330. We found that the soil water content and aging (21 days) had no effect on the recoveries (>92%) of CL-20, provided that the extracts were kept acidic (pH 3). The aqueous solubility of CL-20 was poor ($3.6 \, \mathrm{mg \, l^{-1}}$ at $25\,°C$) and increased with temperature to reach $18.5 \, \mathrm{mg \, l^{-1}}$ at $60\,°C$. The octanol–water partition coefficient of CL-20 ($\log K_{OW} = 1.92$) was higher than that of RDX ($\log K_{OW} = 0.90$) and HMX ($\log K_{OW} = 0.16$), indicating its higher affinity to organic matter. Finally, CL-20 was found to decompose in non-acidified water upon contact with glass containers to give NO_2^- (2 equiv.), N_2O (2 equiv.), and $HCOO^-$ (2 equiv.). The experimental findings suggest that CL-20 should be less persistent in the environment than RDX and HMX.

1. Introduction

   Past and present high-scale manufacturing, use, and disposal of explosives have resulted in severe environmental contamination [1]. Explosives such as the cyclic nitramines, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) (Fig. 1), are toxic to various terrestrial and aquatic receptors [2,3], and the provision of chemical and analytical data on their transport and transformation mechanisms in soil has been the subject of extensive study. Due to their high energy content, polynitropolyaza-caged compounds seem more attractive than the presently used RDX and HMX. A typical energetic chemical of this family is 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane or hexa-nitrohexaazaisowurtzitane (HNIW), commonly known as CL-20 (Fig. 1), which was synthesized by Nielsen [4] and later adopted by Thiokol for pilot scale production [5]. Because of its superior ballistic, detonation and explosive performance, CL-20 may soon replace RDX and HMX.

However, to limit the consequences of its use, the environmental fate, transport and impact of CL-20 should first be thoroughly understood.

   Prediction of the environmental fate (transport and transformation) of a new chemical such as CL-20 requires accurate analysis of the compound and its degradation products in both water and soil samples. The stability of the compound while being manipulated and analyzed should be well characterized. Moreover, physico-chemical parameters such as the octanol–water partition coefficient (K_{OW}), the aqueous solubilities and the soil sorption coefficients (K_d) must become known in order to foresee both bioaccumulation in terrestrial and aquatic biota and migration through subsurface soil that causes groundwater contamination [6]. CL-20 is a relatively new compound and most of its physico-chemical parameters have yet to be determined. The objectives of the present study were threefold: first, to provide the reader with an optimized analytical method to quantify CL-20 in aqueous and soil matrices; second, to make data available on its aqueous solubility at different temperatures (5–60 °C) as well as its octanol/water partition and soil sorption coefficients; and finally, to provide insight into the stability of CL-20 in water.

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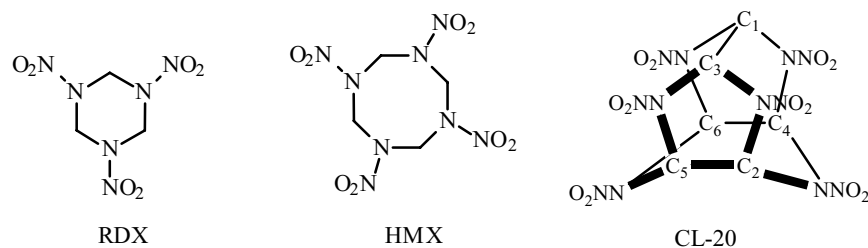 *E-mail address:* jalal.hawari@cnrc-nrc.gc.ca (J. Hawari).

Fig. 1. Structural formulae of nitramine explosives (for clarity protons are omitted).

2. Experimental

2.1. Materials

CL-20 (purity 99.3%, determined by HPLC) was obtained from A.T.K. Thiokol Propulsion (Brigham City, UT, USA), as an ε-form (≥95% as determined by IR). Elemental composition was determined on a Carlo Erba EA 1108 analyzer and was found to be C (16.84%), N (37.52%), H (1.06%) (calculated values for $C_6H_6N_{12}O_{12}$: C (16.45%), N (38.36%), H (1.38%)). RDX and HMX (with a purity >99%) were provided by Defense Research and Development Canada (DRDC), Valcartier, Que., Canada.

Hydroxypropyl-β-cyclodextrin (HP-β-CD) and heptakis-2,6-di-*O*-methyl-β-cyclodextrin (DM-β-CD) were obtained from Aldrich. Reagent grade inorganic chemicals (CaCl$_2$, NaHSO$_4$, H$_2$SO$_4$) were used as well as deionized Milli-Q^{UV} plus (Millipore) water. The solvents used were acetonitrile (CH$_3$CN, HPLC grade) and methanol (CH$_3$OH, HPLC grade) from J.T. Baker, acetone (CH$_3$COCH$_3$, HPLC grade) from Fisher and octan-1-ol from Aldrich.

The soil (Sassafras Sandy Loam, referenced as SSL) was sampled in an uncontaminated open grassland on the property of US Army Aberdeen Proving Ground (Edgewood, MD, USA). It has a particle size distribution of 11% clay (<2 μm), 18% silt (2–53 μm), and 71% sand (>53 μm), a pH of 5.1, a cation exchange capacity of 5.0 meq./100 g and a total organic carbon content of 0.33%.

2.2. HPLC analysis of CL-20

CL-20 stock standard solutions (10 g l^{-1}) and intermediate standard solutions (100, 10, 1, 0.1 mg l^{-1}) were prepared in acetonitrile and stored at 4 °C in 16 ml glass tubes equipped with PTFE-coated screw caps and wrapped with aluminum. Calibration standards at a minimum of five concentrations (0.05–25 mg l^{-1}) were prepared by diluting the intermediate standard solutions to yield solutions containing acidified water (0.2 g l^{-1} sodium bisulfate) and acetonitrile in a 50:50 (v/v) ratio.

Aqueous samples were diluted with acidified (250 μl concentrated H$_2$SO$_4$ l^{-1}) CH$_3$CN to give a CH$_3$CN–water (50:50 (v/v)) mixture. If analysis could not be performed on the day of preparation, samples were stored at 4 °C away from light.

For soil samples, US Environmenal Protection Agency (EPA) SW-846 method 8330 [7] was used with slight modification. Dried soil (2.0 g) was weighed into 16 ml glass tubes with PTFE-lined caps. Samples and associated quality-control samples were spiked with surrogate (RDX) and CL-20 solutions in acetone to get concentrations of CL-20 in soil ranging from 1 to 10 000 mg kg^{-1}. Solvent was allowed to evaporate overnight in the fume-hood before subsequent extraction by CH$_3$CN (10 ml/each tube) using sonication at 20 °C for 18 h. After centrifugation at $1170 \times g$ for 30 min, a volume of supernatant (5 ml) was combined with 5 ml of a CaCl$_2$–NaHSO$_4$ aqueous solution (5 and 0.2 g l^{-1}, respectively) instead of the usual solution of calcium chloride. The resulting sample was shaken, allowed to stand for 30 min and filtered through a 0.45 μm Millipore PTFE filter, discarding the first 3 ml. The filtrate was analyzed by HPLC.

In order to assess the effect of water on the extraction efficiency, some samples were supplemented with water (0.353 ml (15% (w/w)) or 2 ml (50% (w/w))) following acetone evaporation. One third of the samples were extracted immediately, a second third after being stored at 10 °C and in the dark for 7 days, and the final third after being stored for 21 days under similar conditions.

The CL-20 concentration was analysed by HPLC using a chromatographic system (ThermoFinningan, San Jose, CA, USA) composed of a Model P4000 pump, a Model AS3000 injector, including temperature control for the column, and a Model UV6000LP Photodiode-Array Detector. The separation was completed on a Supelcosil LC-CN column (25 cm × 4.6 mm, 5 μm; Supelco, Oakville, Canada) maintained at 35 °C. The mobile phase (70% aqueous methanol) was run isocratically at 1 ml/min for the entire run time of 14 min. The detector was set to scan from 200 to 350 nm. Chromatograms were extracted at a wavelength of 230 nm with quantification taken from peak areas of external standards. Peaks were identified by comparison with elution times for external standards and UV spectra. The injection volume was 50 μl.

The concentrations of RDX and HMX were determined using a reversed-phase HPLC connected to a photodiode array detection (DAD) system, as described previously for RDX [8].

2.3. Determination of aqueous solubility as a function of temperature

The solubilities (S) of CL-20, RDX and HMX were determined in water at temperatures (T) of 5, 10, 15, 20, 25, 30, 40, 50 and 60 °C according to the procedure described by Lynch et al. [9]. An excess amount of explosive (0.015 g) was added to 100 ml of deionized water (pH 5.5) in a glass bottle. The samples were stirred at 200 rpm and at the required temperature in a thermostated bath (Innowa 3000 (New Brunswick Sci.)), away from light. After a 48 h stirring period, the suspension was filtered and diluted 1:1 in acidified acetonitrile (pH 3). The resulting solution was analyzed by HPLC. All experiments were performed in triplicate.

The solubility of CL-20 was also measured in the presence of two cyclodextrins (CDs): hydroxypropyl-β-cyclodextrin (HP-β-CD) and heptakis-2,6-di-O-methyl-β-cyclodextrin (DM-β-CD). An excess of CL-20 (300 mg l^{-1}) was combined with increasing concentrations of cyclodextrin (0–5% (w/v)) and solubility was measured after 18 h of equilibration at room temperature (21 ± 2 °C).

2.4. Determination of n-octanol/water partition coefficient

Partition coefficients were measured at 21 ± 2 °C as described in the OECD Guideline 107 [10]. A preliminary K_{OW} measurement was done with RDX to check the need to saturate octanol with water and water with octanol before doing the actual measurement. Similar results were obtained with saturated (log K_{OW} = 0.90) and non-saturated (log K_{OW} = 0.90) solvents. Thus, the measurements were performed with non-saturated solvents. Various volumes (3 or 4 ml) of an aqueous solution of explosive (CL-20: 3.48 mg l^{-1}; HMX: 4.01 mg l^{-1}; RDX: 11.20 mg l^{-1}) were added to octan-1-ol (2 or 3 ml) in a 16 ml PTFE-lined capped glass tube. The mixtures were equilibrated for four 10 min shaking periods spaced 10 min apart. The tubes were centrifuged for 10 min at 1170 × g. The concentration of the substrate in water was determined by HPLC as described above. The octanol fraction was diluted (1:3) with a solution containing 70% methanol in water and the concentration of CL-20 was determined by HPLC. Experiments were run in triplicate.

2.5. Determination of RDX, HMX and CL-20 K_d values with SSL soil

Batch sorption experiments were conducted at ambient temperature (21 ± 2 °C) for 72 h. A solution (15 ml) of RDX, HMX or CL-20 (0.5–40 mg l^{-1} for RDX; 0.5–4 mg l^{-1} for HMX and CL-20) was agitated with 2 g dried SSL soil in a 16 ml borosilicate centrifuge tubes fitted with PTFE-coated screw caps, away from light and at 430 rpm (Model 75 Wrist Action shaker; Burrell, Pittsburgh, PA, USA). After centrifugation at 1170 × g for 30 min, the supernatant was filtered through a Millex-HV 0.45 μm filter (Millipore, Bedford, MA, USA), and analyzed by HPLC after discarding the first 3 ml. The remaining pellet was extracted with acetonitrile to measure the amount of sorbed explosive. The respective isotherms (i.e. sorbed amount in μg g^{-1} as a function of the equilibrium concentration in mg l^{-1}) were plotted and the K_d values were obtained from the slopes of linear isotherms.

2.6. Stability of CL-20 in solution

The stability of CL-20 was determined in aqueous and aqueous acetonitrile solutions as a function of temperature. In aqueous acetonitrile media, the solutions (2.5 mg l^{-1}) were allowed to sit at either 10 °C or ambient temperature (21 ± 2 °C) for 7 days and samples were periodically analyzed for CL-20 by HPLC. In water, the solutions (3.5 mg l^{-1}) were agitated in PTFE-capped glass headspace vials at 150 rpm at either 30 °C or ambient temperatures (21 ± 2 °C). Vials were sampled periodically over 14 days to measure the suspected CL-20 degradation product N_2O in the headspace and other products such as nitrite (NO_2^-), nitrate (NO_3^-) and formate ($HCOO^-$) in the liquid. N_2O analyses were carried out as described by Sheremata and Hawari [11]. Analyses of nitrite, nitrate and formate were performed by ion chromatography (IC) equipped with a conductivity detector. The Waters IC system consisted of a Model 600 Pump, a Model 717 Autosampler Plus, and a Model 430 conductivity detector. Separation was performed on a Dionex IonPac AS15 column (250 mm × 2 mm). The mobile phase was 30 mM KOH (aq.) at a flow rate of 0.4 ml min^{-1} at 40 °C. The detection of anions was enhanced by reducing the background with a Model DS-Plus autosuppressor from Altech. Detection limits were 150 ppb.

In another experiment, the stability of CL-20 in water was measured at ambient temperature (21 ± 2 °C) using two types of frequently encountered container materials (glass or polypropylene), under static or agitated conditions. The aqueous CL-20 solution was added to either 16 ml borosilicate centrifuge tubes fitted with PTFE-coated screw caps, or 15 ml polypropylene centrifuge tubes. All tubes were wrapped in aluminum foil. Half the tubes were then agitated on a Wrist Action shaker at 430 rpm (Burrell), while the other half were allowed to remain static. Tubes were sampled periodically over 28 days for analysis by HPLC. These experiments were conducted in triplicate.

3. Results and discussion

3.1. Quantification of CL-20 in aqueous and soil samples

Because explosives are often applied as mixtures, it is important to establish conditions that permit a good separation amongst CL-20 and other energetic chemicals. Analysis by HPLC of a mixture containing RDX, HMX and CL-20 using the previously mentioned conditions gave a well resolved chromatogram with retention times of 4.8, 5.9 and 8.3 min, respectively (Fig. 2). Peak areas were used
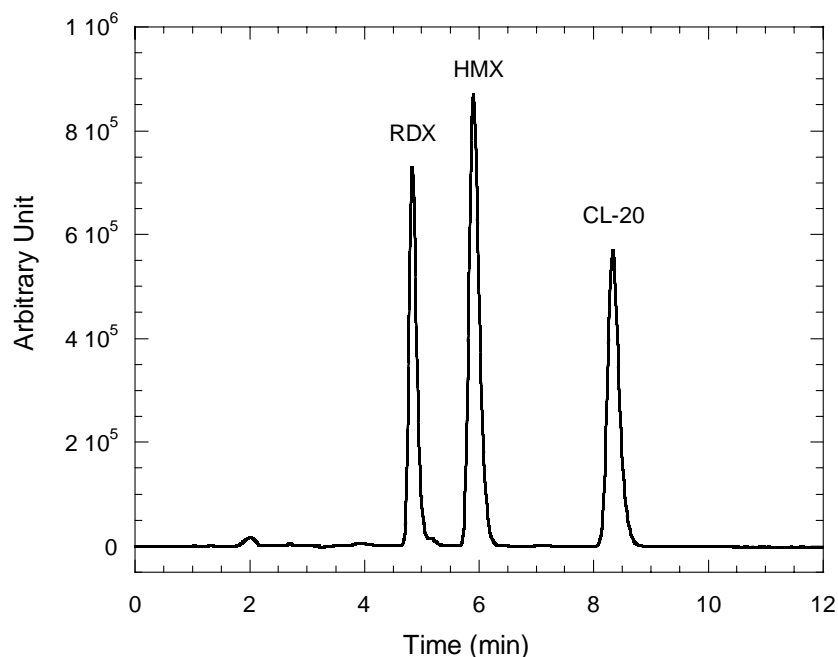
Fig. 2. A typical HPLC chromatogram showing separation of CL-20 from RDX and HMX. Column: LC-CN; mobile phase: water–methanol (30:70); flow rate: $1 \, ml \, min^{-1}$; detection: DAD ($\lambda = 230 \, nm$).

to quantify chromatographic signals and excellent linearity was obtained over the entire range of CL-20 concentrations used (0.05–25 mg l^{-1}) ($y = 6.4864 \times 10^5 x$; $R^2 = 0.99996$). The instrumental detection limit (IDL) and the instrumental quantification limit (IQL) were found to be 3 and 9 μg l^{-1}, respectively (R.S.D. = 3.8%, $n = 10$).

Larson et al. [12] recently published an HPLC method for analyses of CL-20 in water and soil samples but the susceptibility of CL-20 to decomposition has not been reported. For instance, we found that CL-20 degrades significantly in aqueous acetonitrile media (Fig. 3), and that degradation is more rapid at 21 °C (65% after 7 days) than at 10 °C (8% after 7 days). We also found that decomposi-

Fig. 3. Effect of acidification and temperature on the stability of CL-20 in water/acetonitrile (50/50) media.

tion can be significantly reduced by acidifying the medium to pH 3 (Fig. 3). Therefore, in order to avoid a possible degradation of CL-20, all aqueous samples should be analyzed after a 50:50 (v/v) dilution with acidified CH$_3$CN. CL-20 is a weak acid that, upon losing one of its labile protons, can undergo successive degradation steps. It hydrolyses in water under rather mild alkaline conditions. Since acetonitrile is known to be a more powerful proton acceptor than water [13], it may favor the initial deprotonation of CL-20 and hence cause decomposition even in neutral media. Acidification of the media prevents the removal of the labile proton from CL-20, thereby stabilizing the chemical.

In the case of soil samples, extraction was performed as described in US EPA SW-846 method 8330 [7]. As a consequence of the instability of CL-20 observed in aqueous acetonitrile media, the extract was added to a solution of CaCl$_2$ containing 0.2 g l^{-1} of sodium bisulfate to bring the solution pH to 3. The method detection limit (MDL) and the method quantification limit (MQL) were determined and found to be 0.06 and 0.20 mg kg^{-1}, respectively ($n = 10$; R.S.D. = 10.7%). CL-20 recoveries were found to stand within the interval 83% $< R <$ 113% ($n = 20$, S.D. = 4.9%, average = 97.9%).

Single laboratory precision method and recovery data are gathered in Table 1 for soil samples spiked with different concentrations of CL-20. Precision was good for replicate analyses and excellent recoveries (96–106%) were obtained over a wide range of concentrations. The addition of water (0, 0.353, or 2 ml of water, corresponding to soils containing 0, 15, or 50% moisture) did not affect the extracted amounts
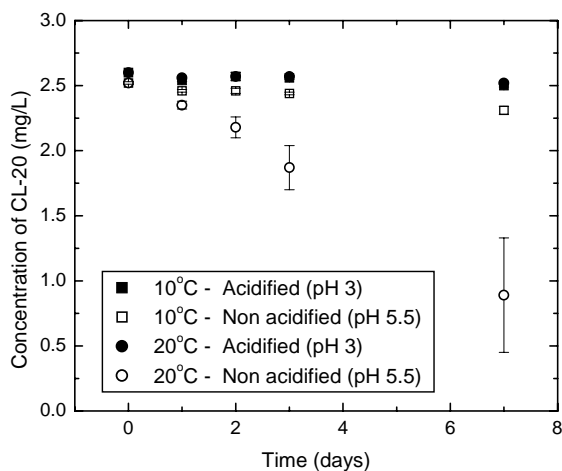
Table 1
Recovery data for soil samples spiked with different concentrations of CL-20

Nominal concentration (mg kg^{-1})	Water (%)	Measured concentration (mg kg^{-1})	S.D. ($n = 3$)	R.S.D. (%)	Mean recovery (%)
1.00	0	1.040	0.156	14.990	104.0
	15	1.015	0.021	2.041	101.5
	50	1.000	0.028	2.771	100.0
5.00	0	5.107	0.535	10.477	102.1
	15	5.166	0.062	1.202	103.3
	50	5.300	0.080	1.508	106.0
10.00	0	10.373	0.211	2.037	103.7
	15	10.156	0.188	1.855	101.6
	50	10.400	0.126	1.212	104.0
100.00	0	99.247	1.385	1.396	99.2
	15	99.354	1.078	1.085	104.0
	50	101.656	0.321	0.315	101.7
1000.00	0	978.733	6.481	0.662	97.9
	15	994.578	11.404	1.147	99.5
	50	1001.720	15.574	1.555	100.2
10000.00	0	10261.667	137.114	1.336	102.6
	15	9669.702	394.638	4.081	96.7
	50	9978.400	334.422	3.351	99.8

of CL-20. No degradation of CL-20 occurred when adding 2 ml of water to the 10 ml of acetonitrile and sonicating the mixture for 18 h at 20 °C, thus demonstrating the applicability of the method to both dry and wet samples. Aging (21 days) of spiked samples with 0 or 15% water showed that CL-20 extractability was not affected and that irreversible binding did not occur within this period of time.

3.2. Solubility of CL-20 in water

The aqueous solubility (S) of RDX and HMX has been shown to vary significantly with temperature [9,14]. Since the temperatures to which explosives are exposed in the environment may vary from below 0 to greater than 50 °C, the solubility of CL-20 was measured in water over a temperature range of 5–60 °C. For comparison, aqueous solubilities of RDX and HMX were also measured under similar conditions. The solubility data collected are gathered in Table 2. As with RDX and HMX, the aqueous solubility of CL-20 increases with the temperature, but to a lesser extent. The solubility of CL-20 is much lower than that of RDX, whereas the comparison with HMX is more complex: CL-20 is more soluble than HMX at lower temperatures but the trend is reversed at temperatures above 20 °C.

For ideal solutions, the amount of a compound, B, present in solution at saturation can be estimated using Eq. (1).

$$\ln x_{\mathrm{B}} = - \left(\frac{\Delta H_{\mathrm{fus}}}{R} \right) \left(\frac{1}{T} - \frac{1}{T^*} \right), \tag{1}$$

where x_{B} is the mole fraction of solute B, ΔH_{fus} the enthalpy of fusion of solute B, R the ideal gas constant, T the temperature at which equilibrium is considered and T^* the melting temperature of solute B. While aqueous solutions

of explosives are not ideal, the relationship between S and T follows Eq. (2) as described by Lynch et al. [9]:

$$\ln S = A - \frac{B}{T}, \tag{2}$$

where S is the solubility and A and B are arbitrary constants.

Data were thus plotted as $\ln S$ versus $1/T$ (with T (in K)) and linear regressions were performed for the three explosives as shown in Fig. 4. The lower slope observed for CL-20 suggests that this compound has a smaller enthalpy of melting than either RDX or HMX. The linearization allowed comparison of the data from the present study to those reported previously for temperatures other than those investigated here. Solubilities for RDX are in good agreement with data reported by Townsend and Myers [14], but are slightly higher than the solubilities recently measured by Lynch et al.

Table 2
Aqueous solubilities (S) of RDX, HMX and CL-20 as a function of temperature and log K_{OW} values measured at ambient temperature

T (°C)	RDX	HMX	CL-20
S (mg l^{-1}) ($n = 3$)			
5	16.01 (±0.16)	1.32 (±0.16)	1.97 (±0.08)
10	22.19 (±0.12)	1.67 (±0.14)	2.12 (±0.04)
15	29.67 (±0.57)	2.27 (±0.09)	2.48 (±0.02)
20	42.58 (±1.32)	3.34 (±0.12)	3.16 (±0.04)
25	56.35 (±1.79)	4.46 (±0.03)	3.65 (±0.04)
30	n.d.	n.d.	4.89 (±0.03)
40	122.94 (±0.94)	11.83 (±0.09)	7.39 (±0.06)
50	n.d.	n.d.	11.62 (±0.01)
60	342.71 (±3.25)	39.69 (±2.24)	18.48 (±0.80)
Log K_{OW} ($n = 9$)			
21	0.90 (±0.03)	0.165 (±0.006)	1.92 (±0.02)

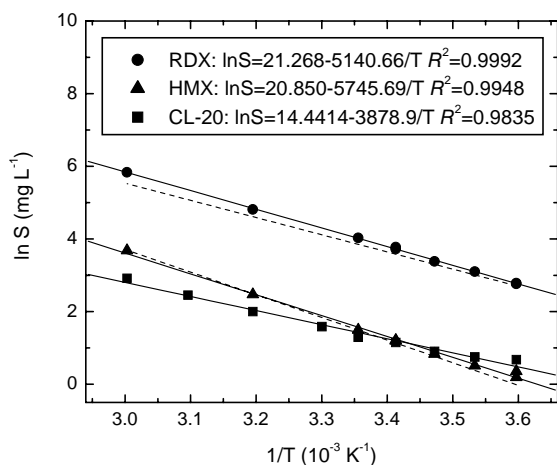Values within parentheses are S.D.; n.d.: non determined.

Fig. 4. Solubilities of RDX, HMX and CL-20 in water as a function of temperature (solid lines: linear regressions from the present study; dashed lines: linear regressions from [9] for RDX and HMX).

[9] represented in dashed lines in Fig. 4. As for HMX, solubility data are consistent with those reported by Lynch et al. [9] and significantly higher than those reported by Spanggord et al. [15]. Overall, the values measured for RDX and HMX agree reasonably well with literature data.

While thinking of a soil washing technology that could be used to remediate a CL-20-contaminated soil, we looked for an environmentally friendly chemical able to increase the solubility of CL-20 in water. Cyclodextrins fit these requirements as they are nontoxic [16] and they were shown to be capable of enhancing the solubility of a number of common organic compounds [17]. The effect of two cyclodextrins (HP-β-CD and DM-β-CD) on the solubility of CL-20 in water was thus studied (Fig. 5). While the presence of both cyclodextrins significantly increased the aqueous solubility of CL-20, the most remarkable effect was induced by DM-β-CD with a 25-fold increase observed when the
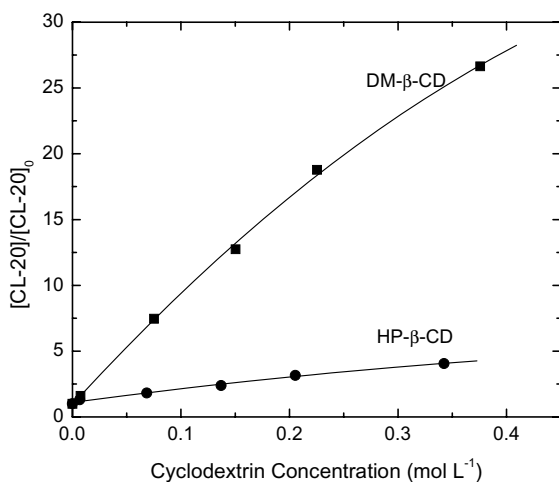
cyclodextrin was present at a concentration of $0.38\,\text{mol}\,\text{l}^{-1}$. In addition to the large solubility enhancement however, we found that DM-β-CD favors the decomposition of the energetic compound as determined by the disappearance of CL-20 in the filtered supernatant (80% loss after 14 days) and the detection of nitrite ions. Therefore, aqueous solutions of cyclodextrins would be more efficient than water to extract CL-20 from a contaminated soil.

3.3. Octan-1-ol/water partition coefficient (K_{OW}) of nitramines

The determination of the octan-1-ol–water partition coefficient (K_{OW}) is of environmental importance because this parameter can be used to predict soil adsorption, migration through subsurface soil and bioaccumulation in terrestrial and aquatic biota. Several log K_{OW} values have been reported for RDX, in relatively good agreement with each other (0.81, 0.86 and 0.87 ([18] and references cited therein)), whereas more disparate values were measured for HMX (0.06 and 0.26 ([18] and references cited therein)). Values of log K_{OW} were measured for RDX, HMX and CL-20 using different combinations of water/octan-1-ol mixtures and different amounts of nitramine. Three different sets of conditions were used for each explosive and each set was run in triplicate. The average of the nine measurements is reported in Table 2. Regardless of the octanol/water ratios used, K_{OW} values remained basically constant and a value of 82.6 ± 0.9 (log $K_{OW} = 1.92 \pm 0.02$) was obtained for CL-20, significantly higher than the partition coefficients for RDX (8.0 ± 0.6) and HMX (1.46 ± 0.02). This finding suggests that CL-20 will sorb onto soils more strongly than RDX and HMX and that this hydrophobic interaction will be particularly important in soils containing high amounts of organic matter. K_d values obtained for RDX, HMX and CL-20 onto SSL soil (0.3, 0.7, and $2.4\,\text{l}\,\text{kg}^{-1}$ for RDX, HMX and CL-20, respectively) confirmed the higher affinity of the latter for soils.

3.4. Stability of CL-20 in water

From the stability results presented in Fig. 6, it appears that agitation in borosilicate glass vials causes greater loss of CL-20 (38% after 17 days) than in agitated polypropylene vials (15% after 17 days). In addition, when the vials remained static at ambient temperature, decomposition decreased (15 and 8% in glass and polypropylene, respectively). We detected nitrite (NO_2^-) and formate ($HCOO^-$) ions in the agitated vials, which we previously detected during the alkaline hydrolysis (pH 10) [19] of CL-20. No CL-20 was recovered from the tubes walls after washing them with CH_3CN, suggesting that no CL-20 sorption took place.

The effect of temperature on CL-20 stability was investigated by agitating sealed head-space glass vials at 150 rpm and either $30\,^\circ\text{C}$ or ambient temperature ($21 \pm 2\,^\circ\text{C}$). Interestingly, 90% of the original CL-20 degraded at $30\,^\circ\text{C}$ after
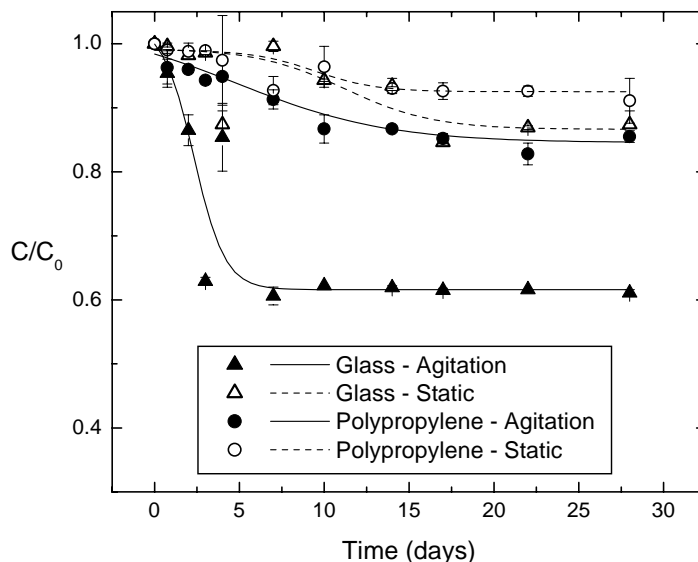

Fig. 5. Solubility of CL-20 in water in presence of β-cyclodextrins, relative to the solubility of CL-20 in water ($[CL-20]_0$).

Fig. 6. Stability of aqueous solutions of CL-20 at ambient temperature ($21 \pm 2\,^\circ$C) in glass and polypropylene containers (static $= 0$ rpm; agitation: 430 rpm).

2 weeks, as compared to 33% at ambient temperature (Fig. 7). Once again, the losses were accompanied by the formation of end products such as nitrite (NO_2^-, ca. 2 equiv.), nitrous oxide (N_2O, ca. 2 equiv.), and formate ($HCOO^-$, ca. 2 equiv.).

The present experimental findings show that CL-20 is unstable and the extent of decomposition depends on the rate of agitation and temperature. The release of 2 mol of NO_2^- ions per mole of reacted CL-20 indicates a partial denitration of the molecule. The detection of 2 mol of $HCOO^-$ ions and 2 mol of N_2O per reacted CL-20 indicates the occurrence of ring cleavage, with a probable initial cleavage at the longer and weaker C_1–C_3 bond between the two cyclopentane rings of CL-20 (1.590 Å compared to 1.575 Å for

C_6–C_4 and C_2–C_5 bonds (Fig. 1)) [20]. These observations are very similar to what was observed in hydrolysis at pH 10 [19], indicating that an initial denitration step is responsible for the lack of stability of CL-20 and its decomposition.

In contrast, neither RDX nor HMX was found to degrade during agitation under the same conditions. However, the polycyclic CL-20 is a more highly strained and thus less stable molecule than are the monocyclic nitramines. Given that nitramine explosives such as RDX are sensitive to friction [21], we suggest that friction obtained during agitation might generate enough energy to cause decomposition of the most sensitive CL-20. With a wetting contact angle of 100.6° in water [22], polypropylene surfaces exhibit a much lower flow friction than borosilicate surfaces (contact angle
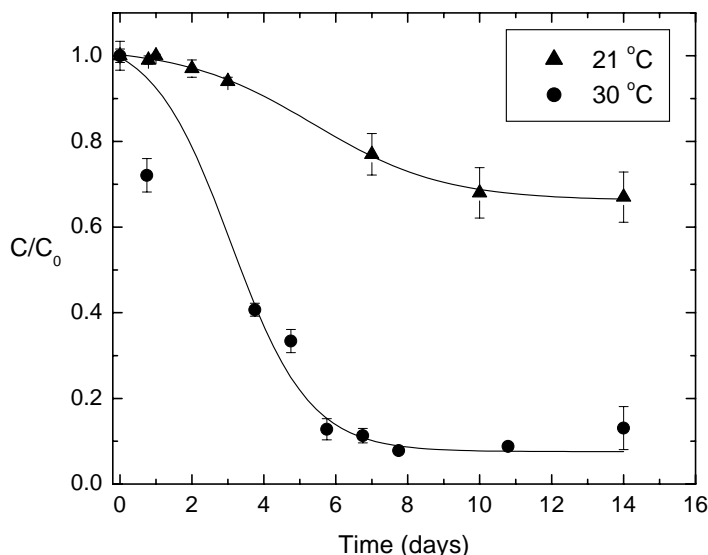

Fig. 7. Effect of temperature on stability of aqueous solutions of CL-20 in glass vials agitated at 150 rpm.

in water: 38.5° [23]). Therefore, the higher stability of CL-20 in polypropylene as compared to borosilicate may result from the lower flow friction, and as a consequence, lower shear force induced in the former. Similarly, heating a solution to 30 °C provides a thermal energy that could enhance the degradation process, explaining why CL-20 degrades faster at 30 °C than it does at ambient temperatures.

4. Conclusion

The present study demonstrates that CL-20 can be extracted from soil samples with high recoveries, regardless of the water content or short-term aging of soil. The poor solubility of CL-20 in water ($2.0\,\mathrm{mg\,l^{-1}}$ at 5 °C and $18.5\,\mathrm{mg\,l^{-1}}$ at 60 °C) and its higher log K_{OW} value compared to those of RDX and HMX (1.92, 0.90, and 0.16, respectively) suggest that CL-20 will migrate less in soil than RDX and HMX. Also, aqueous solutions of CL-20 exhibit significant abiotic losses when agitated in glass containers or when exposed to temperatures above 30 °C. The present experimental findings can be used to provide understanding of the environmental fate of CL-20 that awaits wide scale production and field applications.

Acknowledgements

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