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Cent. Eur. J. Chem. • 12(7) • 2014 • 782–787
DOI: 10.2478/s11532-014-0538-y

Central European Journal of **Chemistry**

Thermal oxidation of irradiated magnetic fluids and their component surfactants and dispersing oils+

RICCCE 18

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Received 2 September 2013; Accepted 18 December 2013

Abstract: Magnetic fluid applications require stability under demanding conditions. Complete magnetic fluids and their component surfactants and dispersing oils were irradiated. Their subsequent thermal oxidation was characterized by chemiluminescence and DSC. Except for polyisobutylsuccinic anhydride, irradiation sensitized the components toward oxidation. The components were ranked by stability. Complete fluids were more stable than would be predicted from their components suggesting that they may be used for nuclear applications.

Keywords: *Magnetic fluids • Oxidation stability • Irradiation • Chemiluminescence • DSC*

1. Introduction

The environment plays an important role in the long term stability of magnetic fluids. Aging affects the colloid stability and altering the chemical structures changes the magnetic behavior. Biomedical and engineering applications require their qualification under various conditions [1].

Magnetic fluid preparation has been extensively reported [2-4]. The stability of the magnetic nanoparticle colloid depends on the surface tension; if the suspending medium is changed the stability decreases [5]. Thus, the preparation method determines the properties and the engineering duty parameters.

Organic suspending media are oxidized during aging, modifying the interactions between magnetic nanoparticles, surfactants, and dispersing oils [6]. Most media contain hydrocarbon structures, so oxidative degradation takes place by a radical mechanism. The main oxidation products contain hydroxyl, carbonyl and acid groups, depending on the initial structures and aging conditions.

Oxidative degradation of magnetic fluids, especially accelerated degradation, has not been reported. This paper examines the effects of prior irradiation on thermal oxidation of some magnetic fluids and their component surfactants and dispersing oils. The results will aid the design of magnetic fluids for use in demanding environments.

2. Experimental procedure

Oleic acids (technical and vegetable grades), lauric acid, myristic acid, transformer oil, vacuum pump oil, octyl stearate, dioctyl adipate, and polyisobutylsuccinic anhydride were obtained from Aldrich. Magnetic fluids were prepared as reported [7].

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\+ *The article has been presented at the 18th Romanian International Conference on Chemistry and Chemical Engineering - RICCCE18 - held in New Montana, Sinaia, Romania on 4-7 S*

The compositions of vegetable grade oleic acid, vacuum pump oil, and transformer oils are complex. Different minor compounds, additives and impurities may also be present in high purity saturated fatty acids and fatty acid esters as well. All organic components were analyzed and used as received.

Aging was performed at room temperature by exposure to 50 kGy of ^{137}Cs γ-irradiation at 0.4 kGy h^{-1}, corresponding to the maximum irradiation during a major nuclear event (except a loss of coolant accident).

Oxidation was characterized by nonisothermal chemiluminescence measurement (LUMIPOL 3, Slovakia) from 25 – 190ºC at 0.2ºC min^{-1}. Sample weights were approximately 100 mg. The results are expressed in counts sec^{-1} g^{-1}, which is independent of sample mass.

Nonisothermal DSC (SETARAM 131 EVO DSC from Setaram Instrumentation, France) was performed in 100 µL aluminum crucibles from 30 – 350ºC at 10ºC min^{-1} under air flowing at 50 mL min^{-1}. Typical DSC parameters and curves characterizing transitions have been discussed [8-10].

3. Results and discussion

The long term stability of organic compounds for use in unexposed areas of nuclear power stations can be evaluated by their γ-irradiation at low dose rate to a maximum of 50 kGy, representing the accumulated dose over about 10 years at the upper limit of exposure. Incident radiation causes the scission of weak bonds and radical formation [11]. The present oxygen reacts and oxidative degradation starts. Further oxidation takes place due to oxygen diffusion into the sample. The oxidation rate depends on the chemical structure, total absorbed dose, dose rate, and sample history [12].

3.1. Chemiluminescence

Excited state carbonyls are formed during the oxidation of organics; subsequent chemiluminescence emission is proportional to their concentration. Thus the chemiluminescence intensity evolution reflects the damage caused by heat, photo-exposure, high energy irradiation, or electrical charge. Increasing the temperature causes progressive oxidation monitored by the variation in chemiluminescence intensity.

In Fig. 1 the behavior of nonirradiated and irradiated materials is compared from nonisothermal chemiluminescence curves. Some principal observations:

- Except for polyisobutylsuccinic anhydride, up to about 100ºC the thermal stability is indistinguishable. The insignificant differences between pristine and irradiated compounds suggest their application in magnetic fluids for nuclear energy areas.
- Polyisobutylsuccinic anhydride shows two CL intensity peaks because different radicals can be generated at the quaternary carbon atoms and double bonds.
- The oxidation of lauric and myristic acids is similar up to 150ºC. The main difference is the maximum oxidation temperature. Lauric acid reaches a maximum intensity around 165ºC, while that for myristic acid exceeds 190ºC.
- Both kinds of oleic acid show similar stability; after irradiation, the radiation stability of vegetable oleic acid is higher than that of technical grade. This may be due to the natural antioxidants in the vegetable grade.
- The presence of two tertiary carbon atoms in dioctyl adipate explains why it is less stable than octyl stearate.
- The greater stability of transformer oil than vacuum pump oil (oxidation start at 175ºC *vs.*125ºC) suggests that it is a better choice.

Table 1. Oxidation onset temperatures (OOT) for magnetic fluid components from CL measurements.

Component	**OOT (ºC)**	
	pristine	**50 kGy**
lauric acid	152	148
myristic acid	154	156
oleic acid – technical grade	157	154
oleic acid – vegetable grade	125	138
dioctyl adipate	146	150
octyl stearate	172	168
vacuum pump oil	167	167
transformer oil	182	183
polyisobutylsuccinic anhydride	100/150	100/153

Table 1 presents the oxidation onset temperatures (OOT).

γ-Irradiation of magnetic fluids induces oxidation. Fig. 2 illustrates typical chemiluminescent behavior of these complex colloidal suspensions. The emission intensity is three orders of magnitude less than those for individual components. The enormous surface of nanoparticles may adsorb the radiolysis intermediates or provide a nonradiative relaxation path, the oxygen penetration depth during irradiation may be less, and the low concentrations of sensitive compounds in the formulations may also explain the differences.

Polyisobutylsuccinic anhydride presents unique behavior. Although the CL intensity measured at 100ºC after irradiation is slightly greater that of the original

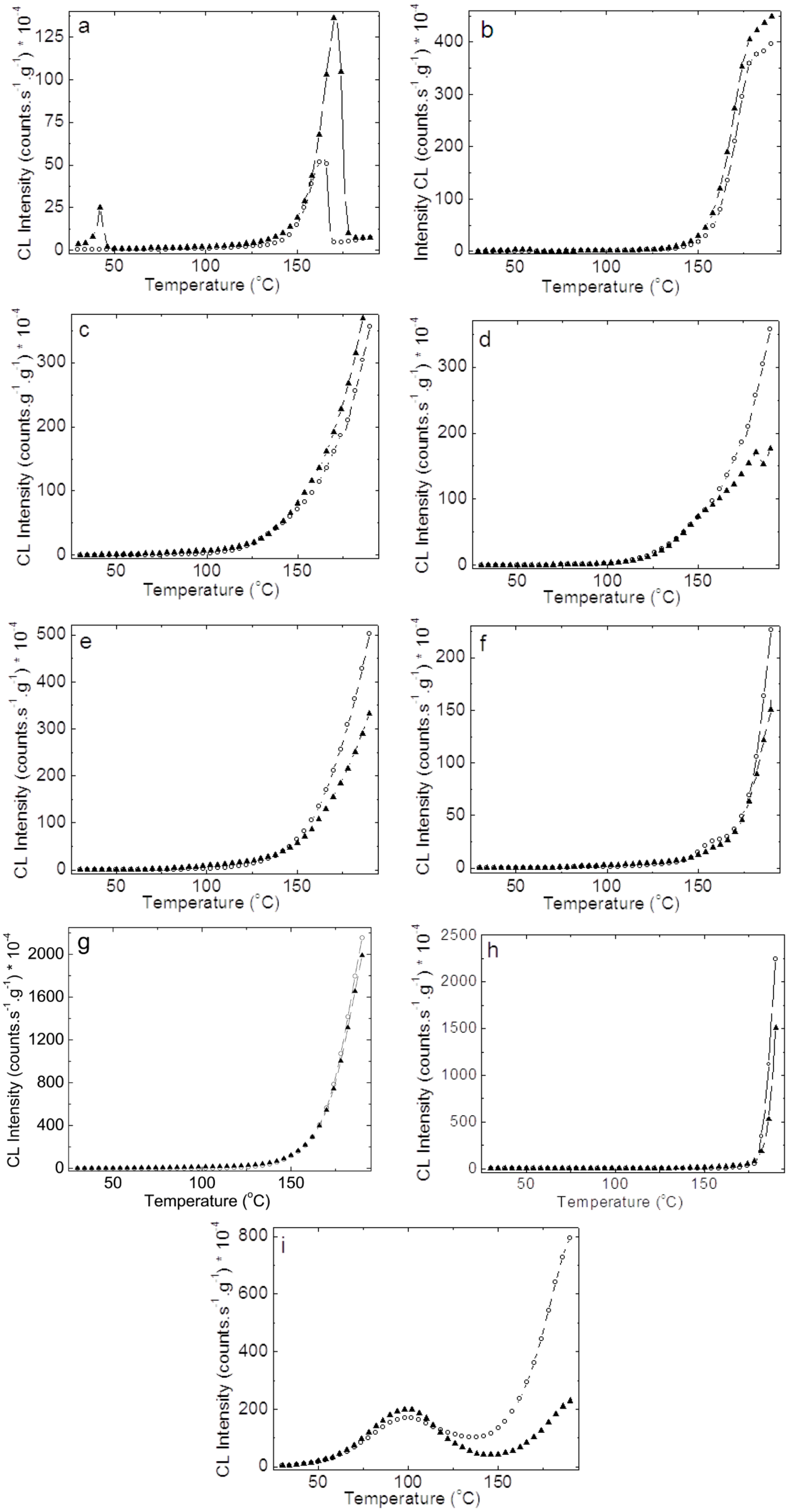

Figure 1. Nonisothermal CL curves for magnetic fluid components. (a) lauric acid; (b) myristic acid; (c) oleic acid – technical grade; (d) oleic acid – vegetable grade; (e) dioctyl adipate; (f) octyl stearate; (g) vacuum pump oil; (h) transformer oil; (i) polyisobutylsuccinic anhydride. (○) pristine sample (▲) 50 kGy irradiated sample.

material, above 125ºC pristine PIBSA shows higher emission intensity than the irradiated sample. Radiation-induced radical crosslinking will preferentially link the butyl groups, reducing the sites available for oxidation [13,14].

Table 2. DSC parameters.

Component	OOT (ºC)	T_{max} (ºC)	ΔH_{ox} (J g^{-1})
Oleic acid (technical)	182.8	269.6	-287
Oleic acid (vegetable)	192.1	252.9	-184
Lauric acid	186.5	228.0	-86
Myristic acid	191.2	231.9	-99
Dioctyl adipate	193.4	256.0	-62
Octyl stearate	203.3	261.0	-199
Vacuum pump oil	200.7	231.0	-45
Transformer oil	241.0	269.6	-45

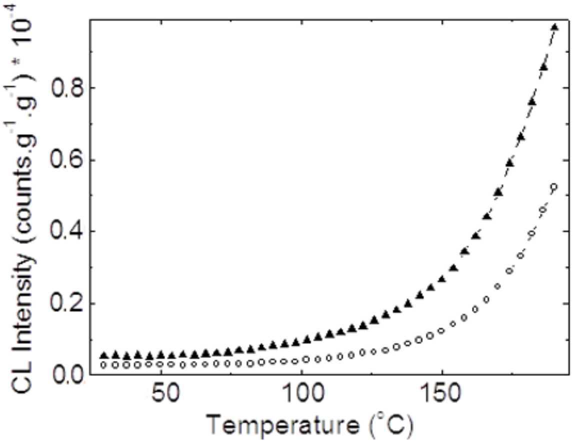

Figure 2. Nonisothermal CL curve for representative magnetic fluid. (○) pristine sample (▲) 50 kGy irradiates sample.

3.2 Differential scanning calorimetry

The organic components contain long hydrocarbon chains. Polar groups (acid or ester) are also present in the surfactants, giving them an amphiphilic character, while for the oils only saturated C-H bonds were present, as shown by the FTIR spectra.

DSC revealed the existence of several processes at low temperatures and of intense exothermic processes above 180ºC. The most important low temperature process is the melting of myristic and lauric acids (Fig. 3). Other low temperature processes are exothermic and peak at 150-160ºC. They can be assigned to thermal decomposition of hydroperoxides formed during storage and heating in air. The most important process at elevated temperature is thermal oxidation starting near 300ºC (Fig. 3). Its kinetic parameters (oxidation onset temperature = OOT, oxidation peak maximum = T_{max}, and thermal effect = ΔH_{ox}) are in Table 2. Because in some cases the oxidation peak was not complete within the scan range, the ΔH_{ox} from Table 2 are all expressed as the heat up to the peak maximum (grey area in Fig. 3).

OOT data in Table 2 indicate that the stabilities decrease roughly: *mineral oils (hydrocarbon mixtures)* > *esters* > *saturated acids* > *unsaturated acids.*

Tables 1 and 2 show that the OOT values found by DSC and CL are different, but the stability order is nearly the same. This difference is due to several factors: (1) the heating rate was considerably lower in CL measurements; transition temperatures shift upward as the heating rate increases; (2) the upper temperature limit of the CL apparatus did not include the entire CL peak resulting in uncertainty in peak location; (3) CL is remarkably sensitive in hydroperoxide detection [18,19]; the small DSC peaks around 150 - 170ºC, assigned to hydroperoxide decomposition could correspond to the increase in CL emission. Precise comparison was not possible because the DSC peaks were wide with

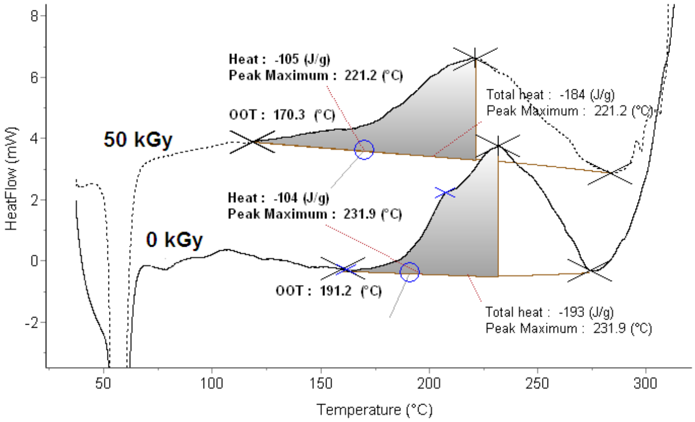

Figure 3. DSC curves for myristic acid (upper, pristine sample and lower, after 50 kGy irradiation).

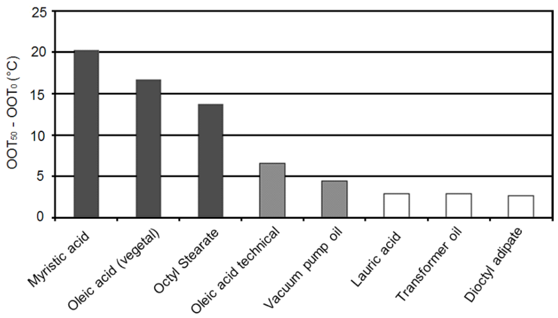

Figure 4. Radiation-induced stability decrease after γ-irradiation at 50 kGy.

several local maxima, but for lauric acid, myristic acid, octyl stearate, and oleic acid (vegetable grade) the CL OOT and DSC T_{max} were reasonably well correlated.

Thermal oxidation occurs by free radical chain reactions initiated by thermal C-H bond scission, followed by propagation and chain termination. An induction period, when no changes in either DSC or CL signal occur, is characteristic of this mechanism. The differences in mechanism, reactivity, induction period, and onset temperature are related to the structure: saturated hydrocarbons which contain only CH_2 groups (linear aliphatic hydrocarbons in dispersing oils) are more resistant than unsaturated molecules [15]. Saturated fatty acids have higher OOT values than oleic acid due to oleic acid's double bond and allylic hydrogen, allowing reaction by both oxidation and polymerization [16,17].

Octyl stearate appears more stable than dioctyl adipate, possibly because it contains fewer oxidation active centers (activated hydrogen atoms near oxygen).

Similar to the CL results, vegetable grade oleic acid is more stable toward thermal oxidation than the technical grade as most of the natural antioxidants (mainly tocopherols [17]) are removed during purification.

The higher OOT for transformer oil than vacuum pump oil can be assigned mainly to oxidation inhibitor (phenol) in the former.

Generally irradiation resulted in a slight decrease in stability evidenced by decreased OOT values. The effect varied as shown in Fig. 4, which presents the OOT decrease. The radiation-induced degradation effect is quite small; from DSC measurements, the highest drop in OOT was for myristic acid. The applied dose (50 kGy) is similar to that used for meat and meat foods sterilization [20]; hence structural changes should be rather small as irradiation was performed in air at a relatively low rate.

The materials can be divided into three degrees of radiation stability (Fig. 4): those with low radiation stability (black), materials with moderate radiation stability (gray) and materials with high radiation stability (white). Although the order of radiation stability is not exactly the same as thermal oxidation stability (see above), materials with high radiation stability have high thermal oxidation stability, while materials with poorer thermal stability also have lower radiation stability.

The occurrence of small radiation-induced change is evident in the infrared spectra, which showed very small changes in the O-H, C-O and C=O regions, corresponding to degradation products such as alcohols, aldehydes, and ketones [20]. In confirmation, the melting points also slightly decreased as illustrated in Fig. 3 for myristic acid.

As the OOT is directly related to the oxidation induction time [21], the OOT values measure oxidation resistance. Oxidation under normal or accidental service conditions (elevated temperatures or ionizing radiation) leads to different oxidation products [22,23] which can degrade the magnetic fluids' self-assembled structures.

Generally, the stability of magnetic fluid to thermal- or radiation-induced oxidation is controlled by the structure of the main organic component (hydrocarbon chain length, unsaturation and branching), the presence of additives and the interactions with the magnetic nanoparticles.

The oxidative stability of the studied magnetic fluids was intermediate between that of the surfactants and the oils used as dispersion media, the OOT values being between 190 and 247°C. This is attributed to complex interactions between the magnetic particles and organic components which can be roughly summarized by:

i) The expected catalytic effect of iron oxide in magnetic particles is partly suppressed because their active centers are blocked by surfactants.

ii) The colloidal self-assembled magnetic particle nanostructure (inorganic core/ organic shell) dispersed in oil reduces surfactant oxidation due to reciprocal blocking of the particle and coating. This suggests that magnetic fluids exhibiting higher oxidation stability should contain more ordered nanostructures than those less oxidation stable.

4. Conclusions

The thermal and radiation stabilities of surfactants used in magnetic fluids place them in an order correlated with their structures. The most important feature is the availability of weaker bonds which can be broken. However, actual magnetic fluids exhibit better than predicted radiation stability, supporting their use in nuclear power plants.

Acknowledgement

This study was performed as part of the National Program (Project 157/2012) funded by the Romanian Agency of Scientific Research.

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