Synthesis of Alkyloxy (di)Alkylamino Propanols, Hydroxy Alkyloxy (di)Alkylamino Propanols, and the Dimer Compounds for Use as Fuel Additives

Pascale Satgé de Caro, Zéphirin Mouloungui*, and Antoine Gaset

Ecole Nationale Supérieure de Chimie de Toulouse, Laboratoire de Chimie Agro-Industrielle - UA INRA, 31077 Toulouse Cedex, France

ABSTRACT: Alkyl glycidyl ethers and bis glycidyl ethers, synthesized in a heterogeneous weakly hydrous medium, were condensed with primary or secondary amines to obtain 3-alkyloxy propanolamines or bis alkyloxy propanolamines in a regioselective manner. The compounds were characterized by conventional spectroscopic methods, and complete nuclear magnetic resonance data are given. Their high-temperature stability, their good emulsifying power, their oxidation, and corrosion inhibition make these compounds suitable for solubilizing ethanol–diesel fuel blends.
JAOCS 74, 235–240 (1997).

KEY WORDS: Alkyloxy alkylamino propanols and dimers, antioxidative properties, cold-flow properties, corrosion inhibition, ethanol–diesel fuel–additive blends, fuel additive, glycidyl ethers, polyfunctional compounds, surface-active agents, viscosity.

Compounds with an acyclic propanic structure have been widely investigated for applications in the pharmaceutical, cosmetics, and food industries. An interesting example is provided by unnatural phospholipids where the propanic moiety is linked to fatty acids and phosphoric acids to confer particular biological properties (1). Other triglyceride derivatives, such as alkyloxy or acyloxy propanolamines with interesting biological and surface-active properties, have also been described (2–5). In the present study, we investigated compounds that combine several key functional groups on the same glycerol structure. Furthermore, the prepared molecules possess different active sites, which also make them attractive as chemical intermediates (6). We propose a synthetic route that leads either to alkyloxy (di)alkylamino propanols or their dimer compounds in two successive steps. The potential of the compounds as polyfunctional fuel additives was also studied. The ethanol–diesel fuel–additive ternary blends tested were found to possess promising properties.

*To whom correspondence should be addressed at Ecole Nationale Supérieure de Chimie de Toulouse, Laboratoire de Chimie Agro-Industrielle-UA INRA, n°31A1010-INPT route de Narbonne 31077 Toulouse Cedex, France.

EXPERIMENTAL PROCEDURES

Materials. Epichlorohydrin (>98%), epibromohydrin (>97%), C_3–C_{16} alcohols, C_2–C_8 diols, potassium hydroxide (>85%, H_2O <15%), polyethylene glycol (PEG 3400), tetraethylene glycol dimethyl ether (TEGDME) (>98%), and C_3–C_{16} alkyl-amines (>97%) were purchased from Fluka (St. Quentin Fallavier, France). Organic solvents (purum for synthesis) were supplied by SDS (solvants, documentation, syntheses) (Bordeaux, France). All reagents were used without further purification.

Analyses. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker (Wissenbourg, France) ARX400 spectrometer (400,134 MHz), with $CDCl_3$ solvent. Signal positions (δ values) were measured relative to the signal for $CHCl_3$ (δ 7.25). ^{13}C NMR $\{^1H\}$ spectra were recorded on a Bruker AC200 spectrometer (50,323 MHz), in $CDCl_3$ solvent. The resonance positions were measured relative to the $CDCl_3$ signal (δ 77.0). ^{15}N NMR $\{^1H\}$ spectra were recorded on a Bruker AM300 spectrometer (30,424 MHz). Signal positions (δ values) were measured relative to the liquid ammonia signal. Infrared (IR) spectra were performed on a 1600 FT-IR Perkin-Elmer spectrophotometer (Norwalk, CT), with a liquid film between KBr plates. Solid compounds were dispersed in KBr discs. Mass spectra were recorded on a HP5989 Hewlett-Packard instrument (Palo Alto, CA) with a chemical ionization detector (ammonia). Compounds were detected in a GC apparatus with a flame-ionization detector (filled column, SE30 on Volasphere; Merck KGaA, Darmstadt, Germany; 100–120 mesh, 2 m, 250°C). A 70–230 mesh silica gel was employed for column chromatography. Satisfactory microanalyses were obtained for all compounds (Carlo Erba elemental analyzer; Rueil Malmaison, France). Thermal analyses were performed with a (Setaram TG-DTG 92 calorimeter (Lyon, France) calorimeter between 25 and 600°C (10°C/min) under nitrogen flow (45 mL/min). Viscosities were measured with a controlled-stress rheometer (Carri-Med CSL 100; Rheo, Champlan, France) with a cone-plate geometry (constraint $\sigma = 2$ N/m^2). Critical micelle concentrations were determined with a Prolabo Tensiomat n3 tensiometer (Prolabo, France). Most of the properties were tested by using standard methods (7).

NF M07-015 = ASTM D 130-80 (Ref. 7). Corrosion tests for oil products. A freshly polished copper strip is immersed in a 30-mL fuel sample for a defined time. Its aspect is compared to an initial strip and noted according to a scale ranging from 1Å to 4°C.

NF M07-42 = EN 116 (Ref. 7). Determination of low flow temperature. A volume of fuel is made to pass through a standard filtering device under decreasing temperature.

NF M07-047 = ASTM D 2274/70 (Ref. 7). Stability of diesel fuel. The fuel remains under oxygen bubbling for 16 h at 95°C. The amount of insoluble materials formed is weighted.

SYNTHESIS OF ALKYL GLYCIDYL ETHERS

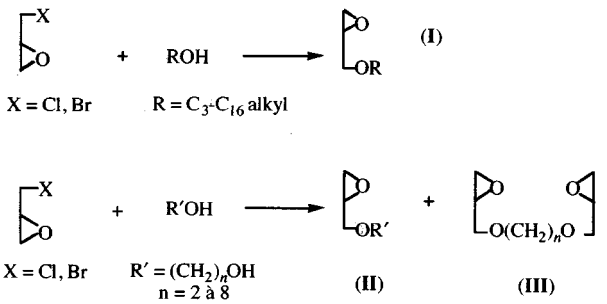
The first step consisted in preparing alkyl glycidyl ethers from epihalohydrin. The literature procedures involved either two steps with an acid-catalyzed reaction, followed by a base-catalyzed one (8,9), or a one-step reaction with a basic agent, such as alkaline hydroxides (10) or alkaline carbonates (11), sometimes coupled with a phase transfer agent (12). In general, these methods presented, respectively, low yields, long reaction times, or costly catalysts that are difficult to remove.

The present method, applied to both mono-alcohols and diols, overcomes many of these drawbacks. The reaction between the alcohol and the epihalohydrin was carried out in a heterogeneous solid/liquid medium (Scheme 1). The solid base (KOH) was dispersed in the weakly hydrous medium. The selected biphasic systems were KOH/hexane for mono-alcohols and KOH/THF for diols.

Glycidyl ether **I** was thus obtained with a 90% yield and a 95% selectivity. The hydroxylated glycidyl ether **II** and its dimer **III** were prepared in proportions ranging from 50 to 85% of **II**, and were readily separated.

The performance of the process for mono-alcohols was improved by using a KOH-PEG/hexane or KOH/TEGDME combination. Under these conditions, reaction yields of 95% were obtained at room temperature with a total selectivity. PEG and TEGDME are good complexing agents for the potassium cations and favor the *O*-alkylation reaction *via* nucleophilic activation from the hydroxide and alkoxy anions that are generated *in situ*.

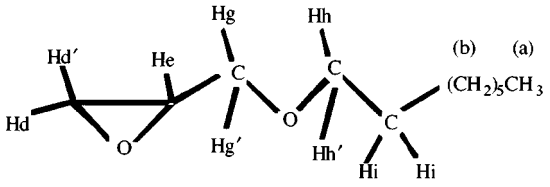
In the first case, hexane is a better vector for reagents toward the basic agent than are oxygenated solvents. In the second case, the diol is the chelating agent itself and is also soluble in tetrahydrofuran.



SCHEME 1

Octyl glycidyl ether (**I**) was prepared by stirring a suspension of epichlorohydrin (1 mol), 1-octanol (118 mL, 0.75 mol) and potassium hydroxide (84 g, 1.5 mol) in 400 mL of refluxing hexane (70°C) for 6 h. After decantation of solid particles (KOH and KCl/KBr) and removal of solvent, the product can be used directly for the second step (90%). The glycidyl ether was purified on a silica chromatography column eluted with Et_2O/hexane 1:1. In experiments in which hexane was replaced with TEGDME (200 mL) or on addition of a PEG, such as PEG 3400 (84 g = the same weight as KOH), the medium was stirred at room temperature for 10 h. Octyl glycidyl ether was then distilled (80°C/0.5 mmHg) to afford 130 g of pure colorless liquid (95%): $C_{11}H_{22}O_2$ (M = 186.23 g/mol), $n_D^{25} = 1.4348$. IR (neat, cm^{-1}):3050 (ν_{CH} epoxide), 1251 (breathing of epoxide), 912 and 848 ($\nu_{a\ C\text{-}O\text{-}C}$ epoxide), 1114 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2927 to 2856 (ν_{CH} CH_2, CH_3), 1466 (δ_{CH} CH_2, CH_3).

^{1}H NMR δ (ppm): 0.8 (*m*, 3 H, H_a); 1.2 (*m*, 10 H, H_b); 1.5 (*m*, 2 H, H_i); 2.5, 2.65 (2 *dd*, 1 H + 1 H, H_d, $H_{d'}$, $J_{d'd}$ = 5.2 Hz, $J_{d'e}$ = 2.3 Hz, J_{de} = 4,7 Hz); 3.25, 3.6 (2 *dd*, 1 H + 1 H, H_g, $H_{g'}$, $J_{g'g}$ = 11.7 Hz, $J_{g'e}$ = 16.9 Hz, J_{ge} = 3.3 Hz); 3.0 (*m*, 1 H, H_e); 3.35 (AA′ part from AA′XX′, 2 H, H_h, $H_{h'}$, J_{AX} = 18.1 Hz, $J_{AX'}$ = 5.7 Hz, $J_{AA'}$ = 14.5 Hz, $J_{XX'}$ = 5.3 Hz) (Scheme 2).



SCHEME 2

The gg′e and dd′e proton groups are 2 AMX systems. The hh′ii′ protons are in AA′XX′ system form. The AA′ part is a 10-peak symmetrical multiplet at 3.35 ppm. The XX′ part is masked by other methylene signals.

^{13}C NMR δ (ppm): 14.1 (CH_3); 22.7 (CH_2-CH_3); 26.0 to 31.7 (CH_2); 44.2 (CH_2 epoxide); 50.8 (CH); 71.5 (O-CH_2); 71.6 (CH_2-O). MS (*m/z*, major peak): 204 (M + 18).

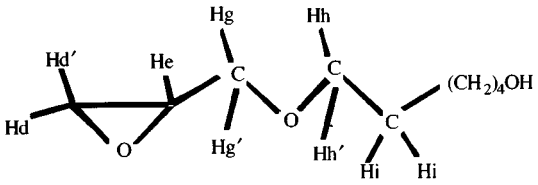
*6-Hydroxy hexyl glycidyl ether (**II**) and 1,6-diglycidyloxy hexamethylene (**III**).* 1,6-Hexanediol (59 g, 0.5 mol) was first dissolved in 100 mL THF. Then, 300 mL of a solution of epichlorohydrin (78 mL, 1 mol) or epibromohydrin (82 mL, 1 mol) and potassium hydroxide (56 g, 1 mol) in THF was added. The medium was stirred under reflux (66°C) for 5 h (epibromohydrin) or 7 h (epichlorohydrin).

After decantation of solid particles (KOH and KCl/KBr) and removal of solvent, the medium was dissolved in chloroform (100 mL), washed with sat. aq. $NaHCO_3$ to remove excess 1,6-hexanediol and finally washed with 4% aqueous HCl to regenerate the alcoholic form of **II**. After elution with hexane/CH_2Cl_2 (2/1) on a silica chromatography column, about 50 g of **II** and 14 g of **III** were isolated.

In subsequent experiments, epibromohydrin was em-

ployed to increase the (**III**)/(**II**) ratio, and the diol was added gradually. After a reaction time of 7 h, 35 g of **II** and 35 g of **III** were obtained: (**II**) $C_9H_{18}O_3$ (M = 174.24 g/mol), (**III**) $C_{12}H_{22}O_4$ (M = 230.30 g/mol). IR (neat, cm^{-1}): 3054 (ν_{CH} epoxide), 1251 (breathing of epoxide), 910 and 852 ($\nu_{a\ C\text{-}O\text{-}C}$ epoxide), 3434 (ν_{OH}), 1060 ($\nu_{C\text{-}O}$ alcohol), 1109 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2930 to 2855 (ν_{CH} CH_2), 1461 (δ_{CH} CH_2).

1H NMR δ (ppm): 1.2 (*m*, 4 H, CH_2); 1.4 (*m*, 4 H, CH_2 β from O and OH); 2.45 and 2.65 (2 *dd*, H_d and $H_{d'}$, $J_{d'd}$ = 5.0 Hz, $J_{d'e}$ = 2.7 Hz, J_{de} = 4.5 Hz); 2.9 (*m*, 1 H, H_e); 3.15 and 3.55 (2 *dd*, H_g and $H_{g'}$, $J_{g'g}$ = 11.5 Hz, $J_{g'e}$ = 5.9 Hz, J_{ge} = 3.0 Hz); 3.3 (*t*, 2 H, H_h and $H_{h'}$); 3.5 (*t*, 2 H, CH_2-OH) (Scheme 3).

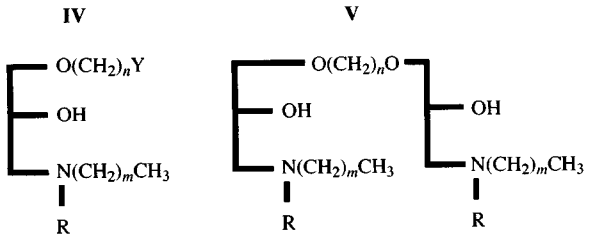


SCHEME 3

The dd′e and gg′e proton groups are two AMX systems: (i) NMR ^{13}C δ (ppm): 25.5, 25.6, 29.5, 32.5 (CH_2), 44.1 (CH_2 epoxide), 50.8 (CH epoxide), 62.3 (CH_2-OH), 71.4 (CH_2-O). (ii) GC–MS (*m/z*): (**II**) 175 (M + 1), 193 (M + 18) and (**III**) 175 ($C_9H_{19}O_3^+$), 248 (M + 18).

SYNTHESIS OF ALKYLOXY PROPANOLAMINES

In a second step, three glycidyl ethers reacted with alkylamines or dialkylamines. Similar reactions had been described in polar protic media, with light amines or light amino-alcohols (13). We propose to extend the method to long-chain amines and to improve selectivity. For secondary amines, the nature of the alcoholic solvent had no influence on the reaction time. The reaction was faster, however, in the presence of excess alkylamine. Glycidyl ethers (**I**, **II**) and (**III**) gave compounds **IV** and **V**, respectively (Scheme 4).

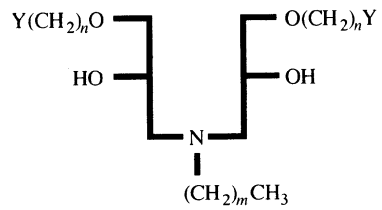


R = H or $(CH_2)_mCH_3$ with *m* = 2 to 15,

SCHEME 4

For primary amines, a third structure **VI** was obtained along with structure **IV** (14). It resulted from a double condensation of the amino moiety on two glycidyl ether molecules, in two successive steps (Scheme 5).

VI



SCHEME 5

To direct the reaction toward the mono-addition compound **IV**, a large excess of amine has generally been employed (15). We found that the amounts of amine could be reduced significantly by a judicious choice of alcoholic solvent (Table 1). Among the three alcoholic solvents, we observed that the mono-addition product was favored in ethanol, while the di-addition product was favored in *tert*-butanol. The role of the solvent appeared to depend on the nature of the hydrogen bonds formed. Ethanol enhances the nucleophilic character of an alkylamine (activating effect) but stabilizes the amino group on the alkylamine alkyloxy propanol structure, effectively impeding formation of the di-addition product.

The mono-addition product **IV** was thus separated from the di-addition product **VI** by crystallizing the latter from the appropriate solvent. Similarly, compound **V** was isolated by crystallization from diethyl ether. This process was successfully transferred to a pilot scale (reactor of 25 L) without altering the experimental conditions.

*1-Octylamino-3-octyloxy-2-propanol (**IV**).* Crude octyl glycidyl ether (200 g, ≈ 1 mol) was added gradually over 2 h to a solution of octylamine (330 mL, 2 mol) in 200 mL of refluxing ethanol (80°C). The reaction was then stirred for 1 h. Excess octylamine and unreacted octanol from the first step were distilled (80–90°C/18 mm Hg). After cooling the crude product, 1-octylamino-3-octyloxy-2-propanol (270 g) was crystallized from pentane as white flakes (90%).

One further hour was required for the reaction with hexadecylamine, and the mono-addition product was isolated from C_{12}–C_{16} alkylamine by crystallization from ethanol: $C_{19}H_{41}O_2N$ (M = 315.53 g/mol), m.p. = 48°C. IR (neat, cm^{-1}): 3414 (ν_{OH} and ν_{NH}), 1110 ($\nu_{C\text{-}O}$ secondary alcohol), 1115 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2925 to 2855 (ν_{CH} CH_2, CH_3), 1465 (δ_{CH} CH_2, CH_3).

TABLE 1
Effect of Nature of Alcohol on the Reaction Orientation

Stoichiometry[a] (OGE/octylamine)	Solvent	pK_a (20°C)	Percentage of major product
1:2	Ethanol	15.9	95
	Isopropanol	17.1	80
	tert-Butanol	19.2	75
2:1	Ethanol	15.9	85
	tert-Butanol	19.2	95

[a]Reagent in excess was added gradually; OGE: octyl glycidyl ether.

1 H NMR δ (ppm): 0.85 (*t*, 6 H, CH_3); 1.25 (*m*, 20 H, CH_2); 1.46 (*m*, 2 H, CH_2 β from N); 1.56 (*m*, 2 H, CH_2 β from O); 2.5 (AA′ part of AA′XX′, 2 H, N-CH_2, $J_{AA'}$ = 13.4 Hz, J_{AX} = 14.5 Hz, $J_{AX'}$ = 3.4 Hz, $J_{XX'}$ = 5.3 Hz); 2.6 (2 AB, 2 H, CH_2-N, J_{AB} = 12.0 Hz, J_{AX} = 2.5 Hz, J_{BX} = 7.5 Hz); 3.35 (2 AB, 2 H, CH_2-O, J_{AB} = 9.8 Hz, J_{AX} = 8.0 Hz, J_{BX} = 9.85 Hz); 3.42 (*dt*, 2 H, O-CH_2); 3.9 (*m*, 1 H, CH, X part of 2 ABX); between 2 and 5 (*br s*, 2 H, OH and NH). ^{13}C NMR δ (ppm): 14.2 (CH_3); 22.7 to 31.7 (CH_2), 49.9 (N-CH_2); 52.2 (CH_2-N), 66.7 (CH); 71.7 (O-CH_2); 73.5 (CH_2-O). ^{15}N NMR δ (ppm): 133.5 (-RN-C_8H_{17}). MS (*m/z*): 316 (M + 1), 204 [316 − 112 ($C_8H_{16}^+$)].

Di[(2-hydroxy-3-octylamino) propyloxy] hexamethylene (V). Either pure **III** or a mixture of **II** + **III** can be used. For instance, 175 g of the mixture, containing about 30% of 1,6-diglycidyloxy hexamethylene (**III**), was added to a solution of octylamine (215 mL, 1.3 mol) in ethanol (250 mL). The solution was stirred for 4 h. The solvent and excess octylamine were distilled (18 mm Hg) before the medium was cooled. **V** was then crystallized from diethyl ether as a white solid (105 g). The co-products dissolved in Et_2O correspond to the **IV** and **VI** structures: $C_{28}H_{60}O_4N_2$ (M = 488.78 g/mol). IR (neat, cm^{-1}): 3346 (ν_{OH},ν_{NH}), 1058 ($\nu_{C\text{-}O}$ secondary alcohol), 1120 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2927 to 2855 (ν_{CH} CH_2, CH_3), 1463 (δ_{CH} CH_2, CH_3). ^{1}H NMR δ (ppm): 0.85 (*t*, 6 H, CH_3, *J* = 6.5 Hz); 1.3 (*m*, 26 H, CH_2); 1.6 (*m*, 8 H, CH_2 β from O and N); 2.6 (AA′ part of AA′XX′, 4 H, N-CH_2, J_{AX} = 15 Hz, $J_{AX'}$ = 3.5 Hz, $J_{AA'}$ = 13.3 Hz, $J_{AX'}$ = 5.2 Hz); 2.7 (AB, 4 H, CH-*CH_2*-N, J_{AB} = 12,0 Hz); 3.4 (*m*, 6 H, CH_2-O); 3.9 (*m*, 2 H, CH); 4,6 (*br. s*, 4 H, OH and NH). ^{13}C NMR δ (ppm): 14.1 (CH_3); 22.6 to 32.6 (CH_2); 49.8, 52.1 (CH_2-N); 68.5 (CH); 71.6, 73.5 (CH_2-O).

N,N-*di-(2-hydroxy-3-octyloxy propyl) octylamine (**VI**).* Octylamine (83 mL, 0.5 mol) was gradually added to a solution of crude octyl glycidyl ether (200 g, ≈ 1 mol) in 200 mL of refluxing *tert*-butanol (85°C) for 2 h. The mixture was then stirred for 1 h. After successive reduced-pressure distillations of octanol and unreacted glycidyl ether, **VI** was obtained as a yellow oil (450 g, 90%): $C_{30}H_{63}O_4N$ (M = 501.82 g/mol), n_D^{25} = 1.45666.

IR (neat, cm^{-1}) : 3428 (ν_{OH}), 1117 (broad, $\nu_{C\text{-}O}$ alcohol, ether), 1108 ($\nu_{a\ C\text{-}O\text{-}C}$ ether), 2925 to 2855 (ν_{CH} CH_2, CH_3), 1466 (δ_{CH} CH_2, CH_3). ^{1}H NMR δ (ppm) : 0.85 (*t*, 9 H, CH_3); 1.25 (*m*, 30 H, CH_2); 1.42 (*m*, 2 H, CH_2 β from N); 1.52 (*m*, 4 H, CH_2 β from O); 2.42 (*m*, 6 H, N-CH_2); 3.40 (*m*, 4 H, CH_2-O); 3.55 (*dt*, 4 H, O-CH_2); 3.8 (*m*, 2 H, CH); between 2 and 5 (*br. s*, 2 H, OH). ^{13}C NMR δ (ppm): 14.1 (CH_3); 22.6 to 32.6 (CH_2); 55.7, 57.8 and 58.1 (CH_2-N); 67.7, 68.2 (CH); 71.1, 71.7 (CH_2-O). MS (*m/z*): 502 (M + 1); 316 ($C_{19}H_{42}O_2N^+$); 130 ($C_8H_{18}O^+$).

RESULTS AND DISCUSSION

Physicochemical properties of the pure compounds were examined. All the alkyloxy propanolamines synthesized exhibited good thermal stability. Table 2 also lists the manner of decomposition according to the thermal lineshape.

TABLE 2
Results of Differential Scanning Calorimetry

Compounds	Temperature of decomposition (°C)	Route of decomposition
IV with R = H, Y = CH_3	320	Oxidation
IV with R ≠ H, Y = CH_3	300	Oxidation
IV with R = H, Y = OH	280	Oxidation
V with R = H, Y = CH_3	300	Polycondensation
VI Y = CH_3	380	Polycondensation

TABLE 3
Critical Micelle Concentrations (CMC) from Measurements of Surface Tension

	Compounds with Y = CH_3, *n* = 7	CMC (mol/L)
At 25°C in EtOH/H_2O (1:1)	**IV** with *m* = 7	1.5 10^{-3}
	IV with *m* = 11	1.1 10^{-3}
	IV with *m* = 15	2.2 10^{-3}
	IV with *m* = 7	2.5 10^{-3}
At 25°C in water	SDS[a]	8.1 10^{-3}
	$C_{10}E_5$[a]	1.0 10^{-3}

[a]SDS, sodium dodecyl sulfate; $C_{10}E_5$: $CH_3(CH_2)_9(OCH_2CH_2)_5OH$.

TABLE 4
Stability of 15% Ethanol Blends with 2% Additive (Y = CH3), Tested Under Influence of a Progressive Increase in Hydration

Blend (10-mL samples)	Duration of blend stability (h)
Without additive	1
IV with *m* = 2 (R = H)	4
IV with *m* = 11 (R = H)	10
IV with *m* = 15 (R = H)	5
IV with *m* = 7 (R = H)	7
IV *m* = 7 (R ≠ H)	5
VI *m* = 7	5

The compounds behaved as surfactants (Table 3), with better critical micelle concentrations than that of the ionic surfactant SDS (16). Our measurements were made in a hydroalcoholic medium instead of water to improve the solubility of the compounds. The presence of an alcohol did not favor micelle formation (17).

The alkyloxy alkylamino propanols were also tested according to specific criteria for fuels. Added to ethanol–diesel fuel blends at 2 wt%, the compounds had lubricant, emulsifying and antioxidative properties, along with inibition of corrosion and an improvement in cold flow.

The molecules had good surfactant power because they prevented the blend from demixing. Table 4 shows that the maximum hydratation rate tolerated by the blend increased in the presence of the additive. These compounds thus behaved as good solubilizing agents for ethanol–diesel fuel blends.

The ability of the functional groups OH and NH to form hydrogen bonds with ethanol was assumed to enhance the cohesion between the hydrous ethanol and the diesel fuel. By the way, intermolecular hydrogen bonds with the solvent molecules have been evidenced by spectroscopic analyses (18).

TABLE 5
Improvement of Viscosity Due to 2% Additive in 15% Ethanol Blends[a]

Addition compounds	20°C (%)	30°C (%)	40°C (%)	50°C (%)
IV	35	15	20	40
V or **VI**	35	25	45	68

[a]Improvement = $100[\eta_2 - \eta_1)/(\eta_0 - \eta_1)]$, calculated with η_0 = viscosity of diesel fuel; η_1 = viscosity of diesel fuel + 15% ethanol; η_2 = viscosity of ethanol–diesel fuel + 2% additive **IV**, **V**, or **VI**.

TABLE 6
Properties of Fuel Blends with 2% Additive IV, V, or VI

Blend without additive	Blend with additive	Properties (Standard test method, Ref. 7)
1B	1A	Anticorrosion (NF M07-015)[a]
8 mg/100 mL	1–1.5 mg/100 mL	Antioxidative (NF M07-047)[b]

[a]Diesel fuel with 15% ethanol + additive.
[b]A standard hydrocarbon base + additive.

Amphiphilic structures are located in the diesel fuel–ethanol interface, enhancing the structural affinity between the components of the blend. The propanolamine moiety represents the hydrophilic head and is oriented toward ethanol, while the hydrophobic part of the structure is represented by the hydrocarbon moiety. A terminal hydroxyl group on the chain (Y=OH) was not, therefore, beneficial to blend stability, but a C_{12} alkyl chain appeared to be optimal (Table 4).

Stable and homogeneous microemulsions were thus prepared with these nonionic surfactants. For instance, an ethanol–diesel fuel blend with 97% ethanol remained limpid with 2 wt% of additive **IV**.

On the other hand, the viscosity of the blend must be high enough to lubricate the injector pump. Addition of 2 wt% of these compounds raised the viscosity of the blend (Table 5). We got similar values for molecules within categories **IV**, **V**, or **VI**. Table 5 also shows that viscosity increased with a rise in temperature between 30 and 50°C. This was accounted for by a polycondensation process, involving the formation of a lubricant film on a metallic surface. This observation is in line with the route of thermal decomposition of compounds **V** and **VI** (Table 2).

The compounds had comparable anticorrosion and antioxidative properties (Table 6). The copper and steel strip samples in contact with the blend that contained additive displayed the 1A standard aspect (light orange) instead of a 1B aspect (dark orange).

Moreover, in the presence of an additive, less insoluble substances, resulting from accelerated oxidation conditions, were detected. The cold flow of the fuel blend was improved compared to that of commercial diesel fuel. These low-temperature flow determinations (NF 07-042) for the 15% ethanol blends with 2% additive, where R = H, Y = CH_3, $m = 7$, $n = 8$, were as follows: commercial diesel fuel (−14°C) blend without additive (−12°C), blend with additive **IV** (−19°C), blend with additive **V** (−14°C), blend with additive **VI** (−18°C). The molecules will tend to possess a better cold flow efficiency as they are good emulsifying agents .

The compounds obtained after a further functionalization reaction also possessed useful properties (19).

In conclusion, these propanic structures were shown to be of interest as multifunctional additives, especially in ethanol–diesel fuel blends. They may also be of value as chemical intermediates for the production of other types of additives.

ACKNOWLEDGMENTS

This work was supported by research grants from ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie) and the Direction de la Recherche RENAULT. We thank E. Poitrat from ADEME and J.C. Griesemann from RENAULT. Financial support was also provided by the Conseil Régional de Midi-Pyrénées.

REFERENCES

1. Guivisdalsky, P.N., and R. Bittman, Glycidyl Derivatives, *J. Org. Chem. 54*:4637–4642 (1989).
2. Laurenzo, K.S., European Patent Applied EP 368 287 (1988).
3. Macchia, B., A. Balsamo, A. Lapucci, F. Macchia, A. Martinelli, H.L. Ammon, S.M. Prasad, M.C. Breschi, M. Ducci, and E. Martinotti, Role of the (Acyloxy)methyl Moiety in Eliciting the Adrenergic β-blocking Activity of 3-(Acyloxy)propanolamines, *J. Med. Chem. 30(4)*:616–622 (1987).
4. Kucharsky, S., Surface Properties and Micelle Formation of *N,N*-di-(2-hydroxy-3-alkoxypropyl)ethanolamine and *N*-(2-Hydroxy-3-alkoxypropyl) diethanolamine Surfactants, *J. Colloid. Interface Sci. 64(2)*:300–310 (1978).
5. Kucharsky, S., Surface and Micellar Properties of *N,N*-di-(2-hydroxy-3-alkyloxypropyl)ethanolamine Surfactants, *Tenside Deterg. 15(2)*:77–82 (1978).
6. Satgé de Caro, P., Synthesis of Polyfunctional Oxygenated Additives for Ethanol–Diesel Fuel Blends, *Thèse INP Toulouse n°1001,* March 1995.
7. Recueil des Normes Françaises AFNOR, Produits pétroliers (Oil products)—Combustibles liquides (Liquid fuels), Association Française pour la Normalisation, Paris, Tome 1, 1988, pp. 121–126; 427–443; 464–467.
8. Pozniak, R., and J. Chlebicki, Synthesis of Higher *N*-(2-hydroxy-3-alkyloxypropyl)ethanolamines and *N*-(2-hydroxy-3-alkyloxypropyl)diethanolamines, *Polish J. Chem. 52(61)*:1283–1288 (1978).
9. Zielinska, E., and D. Gasztych, Synthesis of 1-Chloro-2-hydroxypropyl alkyl and 1,2-Epoxypropyl alkyl ethers, *Rocz. Chem. 49(7–8)*:1405–1409 (1975).
10. Tucker, H., Stereospecific Synthesis of Threo- and Erythro-1-(Aryloxy)-3-(alkylamino) Butan-2-ols, *J. Org. Chem. 44(16)*: 2943–2945 (1979).
11. Honda, K., and Y. Nishijima, JP 54 115 307 (1979).
12. Mouzin, G., H. Cousse, J.P. Rieu, and A. Duffos, A Convenient One-Step Synthesis of Glycidyl Ethers, *Synthesis*:117–119 (1983).
13. Pozniak, R., and J. Chlebicki, Synthesis of Higher *N*-(2-hydroxy-3-alkyloxypropyl)methylamines and *N*-(2-hydroxy-3-alkyloxypropyl) ethylamines, *Polish J. Chem. 54 (3)*:587–590 (1980).
14. Kucharsky, S., Synthesis of *N,N*-di(2-hydroxy-3-Alkoxypropyl) Ethanolamines from Glycidyl Ethers and Ethanolamine, *Rocz. Chem. 81(7–8)*:1337–1344 (1977).
15. Mauléon, D., M. Dolors-Pujol, and G. Rosell, β-Andrenergic Antagonists: *N*-alkyl and *N*-amidoethyl(arylalkoxy)propanol-

amines Related to Propanolol, *Eur. J. Med. Chem. 23*:421–426 (1988).
16. Fendler, J.H., and E.J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975.
17. Green, F.A., Interactions of a Nonionic Detergent: III Hydrophobic Interactions, *J. Colloid Interface Sci. 41(1)*:124–129 (1972).
18. Satgé de Caro, P., Z. Mouloungui, and A. Gaset, Conformational Analysis of Alkyloxy (di)alkylamino propanols by ^{1}H Nuclear Magnetic Resonance and Molecular Modeling, *Bull. Soc. Chim. Belg.*, in press (1997).
19. Z. Mouloungui, and Satgé de Caro, P., French Patent (Renault) FR 95-02187 (1995).

[Received April 1, 1996; accepted November 25, 1996]