Effect of Homolog Distribution on the Toxicity of Alcohol Ethoxylates

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ABSTRACT: Previous work established a high correlation between the potential environmental toxicity of oxyethylenated nonionic surfactants and the average degree of ethoxylation. For this reason, it was considered of interest to determine whether a narrow- or broad-range homolog distribution of polydisperse commercial alcohol ethoxylates would influence toxicity. Ethoxylated fatty alcohols, both linear and branched, were synthesized with sodium hydroxide or an unconventional calcium-based catalyst. Toxicity tests were run on *Daphnia magna* and luminescent marine bacteria. Toxicity of ethoxylated alcohols as a function of type of ethoxylate homolog distribution (narrow or broad) and average degree of polyaddition is analogous for both test species. However, narrow-range ethoxylates show lower toxicity values than conventional ethoxylates. Differences in toxicity values between broad- and narrow-range ethoxylates depend on the degree of ethoxylation.
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KEY WORDS: Alcohol ethoxylates, homolog distribution, toxicity.

Extensive use of ethoxylated fatty alcohols in products of high consumption, such as detergent formulations, cosmetics, and pharmaceutical chemicals, justifies an increasing interest in improving physical characteristics and behavior. Properties of ethoxylated compounds depend not only on the starting alcohol structure and total content of ethylene oxide (EO) units (1), but also on the specific distribution of ethoxylated homologs (2–4), the latter being influenced by the conditions and type of catalyst used for their synthesis (5–8). On an industrial scale, conventional manufacturing processes yield ethoxylated alcohols with a broad distribution of EO homologs. When comparing broad-range distribution homologs (BRD) with those with narrow-range distributions (NRD), the latter contain lower amounts of free fatty alcohol. NRD ethoxylates also contain fewer homologs with higher and lower degrees of ethoxylation. Consequently, physicochemical properties, such as solubility, viscosity, and surface tension, can be different. These differences may translate into distinct advantages in certain applications, examples of which are reduction in pluming during spray drying, more degrees of freedom for liquid formulations, better humectability, and less odor. Thus, for optimizing the efficiency of ethoxylated fatty alcohols, it may be important to produce these products with narrow-range technology, which requires the use of proprietary ethoxylation catalysts.

The main objective of this research was to determine whether the toxicity of ethoxylated alcohols is affected by a broad- or narrow-range EO distribution while taking into account the tight relationship between toxicity and ethoxylation degree of nonionic surfactants reported previously (9,10).

EXPERIMENTAL PROCEDURES

Materials. For the synthesis of ethoxylates, the following hydrophobic substrates were used: *n*-dodecanol (98%); Alfol 1214 (Vista Chemical Co., Austin, TX) (78.5% linear C_{12} alcohol and 20.7% C_{14} linear alcohol) and Lial 125 (Enichem, Augusta, Milan, Italy) (branched alcohol containing 4.6% C_{11}, 20.6% C_{12}, 28.1% C_{13}, 20.6% C_{14}, 5.5% C_{15}, and about 21% isomers). Conventional ethoxylated products (BRD ethoxylates) were obtained with sodium hydroxide as catalyst, whereas NRD ethoxylates were obtained with a calcium-based catalyst, W7^{TM}, commercially produced by the Blachownia Institute of Heavy Organic Synthesis (Kedzierzyn-Kozle, Poland).

Synthesis of ethoxylates. Ethoxylation was performed in a 2-L stainless-steel jacket reactor, equipped with a driven stirrer and a cooling coil. In each process, the reactor was charged with the alcohol substrate and an appropriate amount of catalyst (0.4% W7^{TM} or 0.2% NaOH, with respect to the hydrophobic substrate). Then, the reactor was closed, purged with nitrogen, and heated to the reaction temperature (180 and 135°C for W7^{TM} and NaOH, respectively). After the desired temperature was achieved, EO was admitted to the reactor from a container, which was pressurized with nitrogen at 0.6 MPa. The pressure of EO in the reactor was kept constant by opening or closing a micrometric valve. The reaction mixture was maintained at the set temperature for 30 min.

Proton nuclear magnetic resonance (NMR). Average degree of ethoxylation was determined with a Hitachi Perkin-Elmer (Tokyo, Japan) ^{1}H NMR spectrometer, model R-24A, frequency 60 MHz at 36°C. A sample of 0.1 g ethoxylated alcohol was added to an NMR tube, containing 0.5 mL of

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deuterated chloroform, and shaken well. The tube was placed in the ^1H NMR spectrometer, and spectrum signals were integrated (11).

Homolog distributions of the ethoxylation products were chromatographically determined (12,13). Alcohol ethoxylates with the lowest degrees of ethoxylation were analyzed by gas chromatography, while for alcohol ethoxylates with the highest degrees of ethoxylation a high-performance liquid chromatography (HPLC) procedure was used.

Gas chromatography. Homolog distributions of ethoxylates were determinated with a Perkin-Elmer (Norwalk, CT) model 900 chromatograph, equipped with a flame-ionization detector. Separation was carried out on a stainless-steel column of 0.9 m length and 2.7 mm inner diameter. Chromosorb G-AW-DMCS (60–80 mesh; Celite, Denver, CO) was used as the support, and silica resin OV-17 (Celite) was used as the liquid phase. The weight ratio of liquid phase to support was 1:99. Argon was used as the carrier gas at a flow rate of 15 cm^3/min. Temperatures of the detector and injector were 330 and 340°C, respectively. Analyses were started with a column temperature of 120°C, which was programmed after 1 min at a rate of 4°C/min up to 320°C. All products were analyzed as acetate derivatives.

HPLC. Samples were analyzed on a Hypersil APS-2 column (250 × 2.1 mm; Hewlett-Packard, Waldbronn, Germany) with spherical 5-μm particles and an evaporative light-scattering detector (ELSD) (Varex ELSD II A; Varex, Burtonsville, IN). The mobile-phase solvents were *n*-hexane (A) and a mixture of 5% water in 2-propanol (B). A linear program from 100% A to 40% A and 60% B in 55 min at flow of 0.3 mL/min was used. The ELSD drift tube was heated to 50°C, and the flow of nebulizing gas (nitrogen) was set at 35 mm (1.57 dm^3/minute). The sequence of each sample was determined by comparison of their retention times to those of monododecyl ether standards: penta-, heptaethyleneglycol (Nikko Chemicals, Tokyo, Japan) and nonaethyleneglycol (Fluka, Buchs, Switzerland). The content of each homolog was determined as percentage area of the corresponding peak.

Toxicity tests. Two acute toxicity tests were undertaken. The first was the 24-h inmobilization test with *Daphnia magna* (14); the second was the Microtox^R toxicity test (Microbics Corp., Carlsbad, CA), which employs the luminescent marine bacteria *Photobacterium phosphoreum* (15). In the present work, the Microtox toxicity data are based on 30-min exposure of the bacteria to the surfactant solution at 15°C.

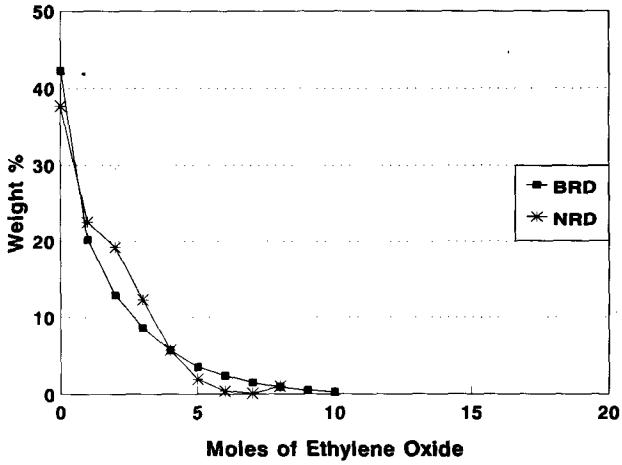

FIG. 1. Narrow- (NRD) and broad-range (BRD) homolog distributions of *n*-dodecanol ethoxylates that contain an average of 1 mole ethylene oxide per mole of alcohol.

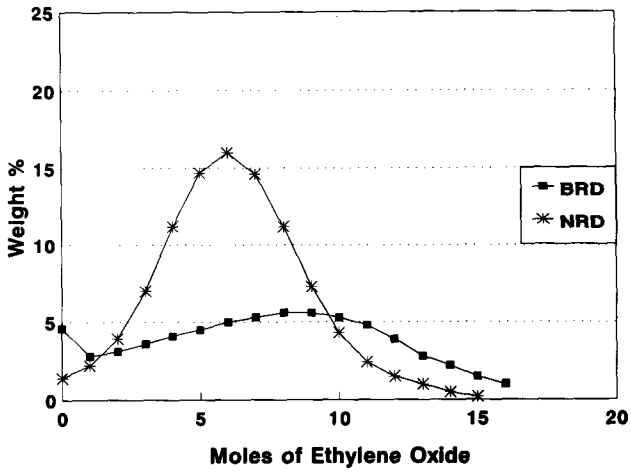

FIG. 2. Narrow- and broad-range homolog distributions of *n*-dodecanol ethoxylates that contain an average of 5.4 moles ethylene oxide per mole of alcohol. See Figure 1 for abbreviations.

RESULTS AND DISCUSSION

Homolog distribution. Typical homolog compositions corresponding to BRD and NRD of ethoxylated dodecanol obtained with NaOH and an unconventional calcium-based catalyst are shown in Figures 1, 2, and 3, respectively. Average degree of ethoxylation increases from 1 to 5.4 to 11 in Figures 1, 2, and 3, respectively. The narrow EO homolog range (also known as "peaking") gives rise to homolog distributions that are characterized, in contrast to conventional ethoxylated mixtures, by a reduction in three species: (i) free alcohol, (ii) low-mole homologs, and (iii) high-mole homologs. The effect of "peaking" on these groups is dependent on the average degree of ethoxylation.

Toxicity of BRD and NRD ethoxylated alcohols. Toxicity of the compounds was determined with both *D. magna* and bioluminescent bacteria. Concentration values that caused 50% inhibition in *Daphnia* mobility (IC_{50}) and 50% reduction in emitted light (EC_{50}) were determined in each test, respectively.

Results are plotted in Figures 4–9. In general, the

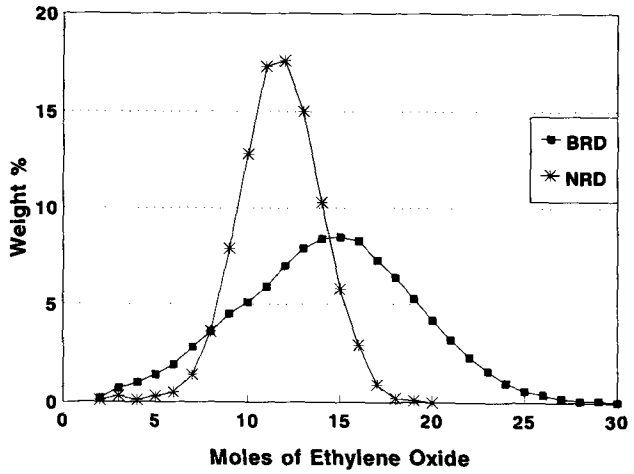

FIG. 3. Narrow- and broad-range homolog distributions of *n*-dodecanol ethoxylates that contain an average of 11 moles ethylene oxide per mole of alcohol. See Figure 1 for abbreviations.

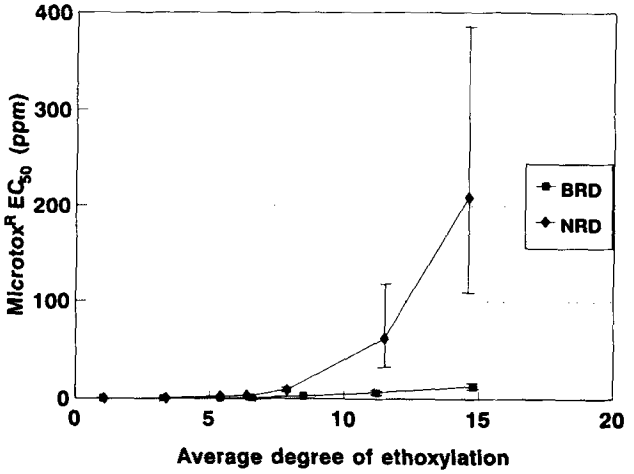

FIG. 5. Luminescent bacteria toxicity vs. average degree of ethoxylation for narrow- and broad-range distribution ethoxylates of dodecanol. See Figure 1 for abbreviations. Microtox^R from Microbics Corp. (Carlsbad, CA). EC_{50}, 50% reduction in emitted light.

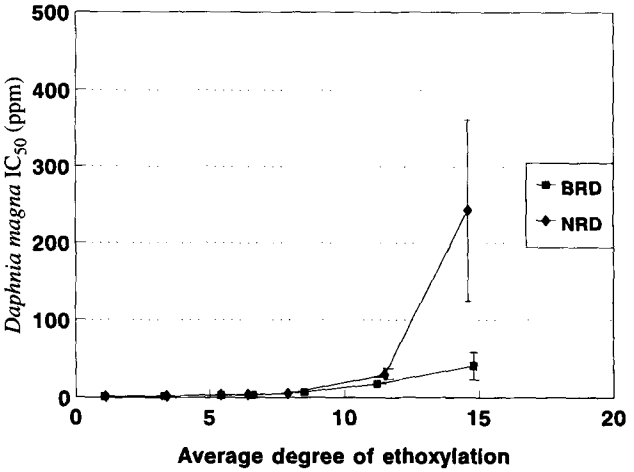

FIG. 4. *Daphnia magna* toxicity vs. average degree of ethoxylation for narrow- and broad-range distribution ethoxylates of dodecanol; IC_{50}, 50% inhibition in mobility. See Figure 1 for other abbreviations.

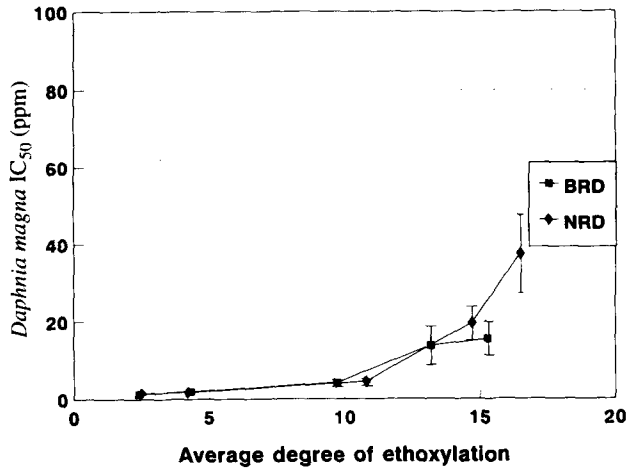

FIG. 6. *Daphnia magna* toxicity vs. average degree of ethoxylation for narrow- and broad-range distribution ethoxylates of Alfol 1214 (Vista Chemical Co., Austin, TX). See Figures 1 and 4 for abbreviations.

ethoxylated fatty alcohols (linear and branched) exhibit significant toxicity for both species when the average ethoxylation degree is lower than 10. It is also generally observed that higher average EO content results in higher effective concentration values (IC_{50} and EC_{50}), meaning that toxicity decreases with increasing hydrophilicity of the molecules.

Regarding the comparative toxicity of BRD and NRD ethoxylates, virtually no differences are seen at low EO levels, while for medium to high ethoxylated products (more than 8–10 EO units) measurable differences are detected. NRD ethoxylates are less toxic than BRD ethoxylates for high average degrees of ethoxylation. Thus, it is shown that "peaking" reduces free alcohol and low-mole homolog levels, which leads to increased hydrophilic character and lower toxicity compared to conventional products.

The linear and branched alcohol derivatives cannot be compared in a straightforward manner because, at equal ethoxylation levels, they have unlike composition due to different average alkyl chainlength.

Alfol ethoxylates are more toxic compared to dodecanol ethoxylates, presumably due to an increased fraction of C_{14} chain moiety.

In relation to the two species tested, toxicity differences between BRD and NRD homologs become detectable at lower average degrees of ethoxylation for the bacteria population. *Daphnia magna* and bacteria are about equally sensitive to *n*-dodecanol-based BRD ethoxylates when compared to NRD analogs (Figs. 4 and 5). However, the bacterial population is more sensitive to BRD ethoxylates of C_{12}–C_{14} linear alcohol and branched alcohol.

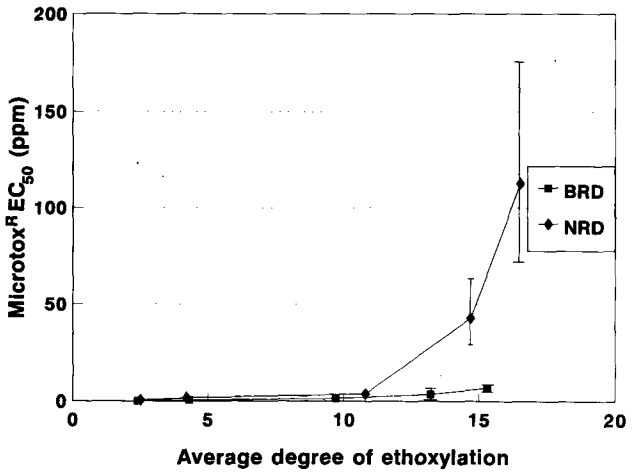

FIG. 7. Luminescent bacteria toxicity vs. average degree of ethoxylation for narrow- and broad-range distribution ethoxylates of Alfol 1214. See Figures 1 and 5 for abbreviations and Figures 5 and 6 for company sources.

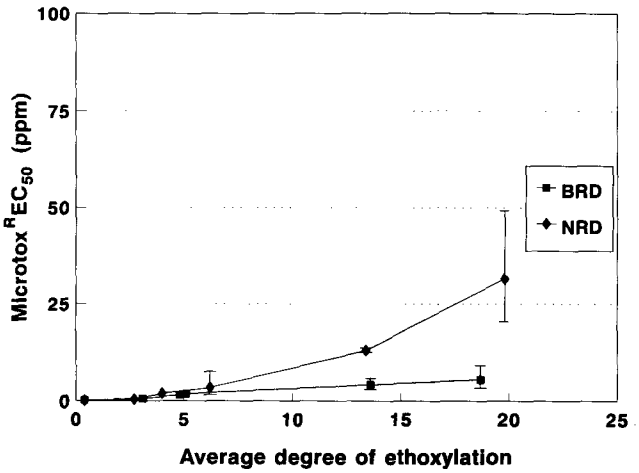

FIG. 9. Luminescent bacteria toxicity vs. average degree of ethoxylation for narrow- and broad-range distribution ethoxylates of Lial 125. See Figures 1 and 5 for abbreviations. See Figures 5 and 8 for company sources.

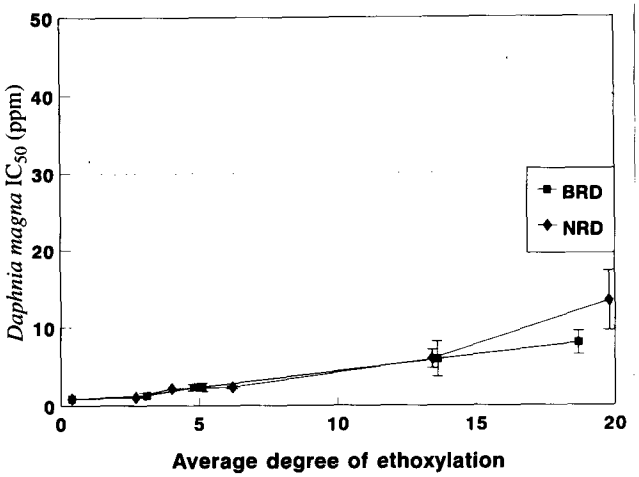

FIG. 8. *Daphnia magna* toxicity vs. average degree of ethoxylation for narrow- and broad-range distribution ethoxylates of Lial 125 (Enichem Augusta, Milan, Italy). See Figures 1 and 4 for abbreviations.

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